ISSN: 2977-0041

Research Article

Journal of Material Sciences and Engineering Technology

Emission of Cluster Ions During Surface Sputtering

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Received: July 21, 2026; **Accepted:** July 28, 2026; **Published:** August 05, 2026

ABSTRACT

Atomic clusters—aggregates of atoms bound by interatomic forces—represent a distinct intermediate state between isolated atoms (or molecules) and bulk solids. Investigating cluster properties provides fundamental insight into the transition from single atoms to the solid state and enables the design of materials with novel chemical and physical functionalities. Clusters can be generated through adiabatic gas expansion, laser evaporation, or surface sputtering induced by ions, electrons, or photons. Despite extensive studies, the underlying mechanisms governing cluster emission under ion bombardment, including the formation of positive and negative clusters and their excited states, remain incompletely understood.

In this work, we present a comprehensive experimental study of cluster ion emission from C, NaCl, Mg, Al, Si, S, Ti, and GaAs surfaces under 0.5–50 keV N^+, O^+, N_2^+, O_2^+, and Ar^+ bombardment. The dependence of cluster yield on size is analyzed, with particular emphasis on small ("light") clusters ($n < 10$), which form via collective atomic motion during collision cascades. Localized energy deposition near the surface may lead to correlated emission of neighboring atoms that remain bound as clusters. These findings provide further insight into the mechanisms of cluster formation and the role of projectile type in ion-surface interactions.

Keywords: Ion Bombardment, Sputtering, Cluster Emission, SIMS, Collision Cascade

Highlights

- Cluster-ion emission under atomic and molecular ion bombardment was investigated experimentally.
- Molecular ion bombardment enhances Al_2^+ and Al_3^+ yields through overlapping collision cascades.
- Cluster emission is interpreted within a correlated sputtering framework based on Sigmund theory.
- Light and large clusters are associated with distinct collisional and thermal emission regimes.
- Experimental results are interpreted using cascade-overlap and thermal-spike-assisted mechanisms.

Emission of Cluster Ions during Surface Sputtering Unified interpretation of cluster formation under atomic and molecular ion bombardment

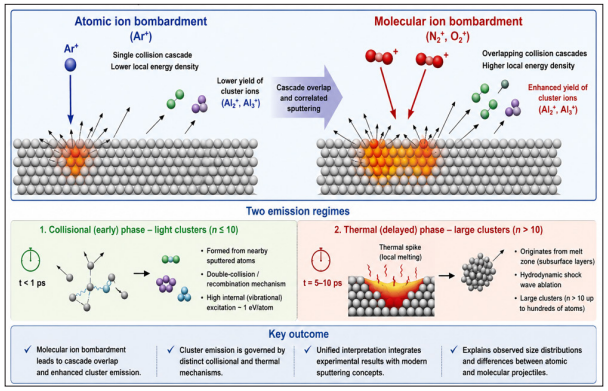

Figure caption: Schematic illustration of cluster-ion emission mechanisms in surface sputtering. Atomic ions produce a single collision cascade with lower cluster yields, whereas molecular ions (N_2^+, O_2^+) generate overlapping cascades, leading to enhanced local energy density and increased emission of Al_2^+ and Al_3^+ clusters. Two emission regimes are distinguished: (1) early collisional phase for light clusters ($n \leq 10$) and (2) delayed thermal phase for large clusters ($n > 10$) associated with thermal-spike-induced ablation.

Citation: George G Meskhi. Emission of Cluster Ions During Surface Sputtering. J Mat Sci Eng Technol. 2026. 4(4): 1-7.
DOI: doi.org/10.61440/JMSET.2026.v4.116

Introduction

The bombardment of a solid by atoms or ions with energies in the keV range leads to the emission of a variety of secondary particles from the surface. It is well established that the sputtered flux consists not only of monatomic target particles, electrons, and radiation over a wide energy range but also—depending on experimental conditions—of a certain fraction of neutral and ionized clusters. Historically, information on the yield and energy distribution of clusters has been obtained mainly from measurements of cluster ions, owing to the experimental difficulties associated with the detection and analysis of sputtered neutral particles [1-3].

Numerous studies have been devoted to the investigation of cluster emission during sputtering, with comprehensive reviews presented in the literature [4-6]. Much of this work has focused on metallic samples as model systems for purely collisional sputtering conditions, and most published data concern charged clusters. Interpretation of experimental results can provide valuable information about the physical and chemical state of the investigated surface, provided that the mechanisms responsible for cluster formation and ejection during sputtering are sufficiently well understood [3,5,27].

Clusters are finite assemblies containing a specific number of atoms, n, referred to as the cluster size. They provide an opportunity to study the evolution of physical and chemical properties from isolated atoms toward the solid state. As the number of atoms increases, clusters acquire increasingly specific properties, making them unique physical objects distinct from both individual molecules and bulk solids [7]. In macroscopic systems, physical properties are independent of sample size; however, when dimensions become sufficiently small, cluster properties depart significantly from bulk behavior and evolve as a function of size. Physical and chemical properties—including geometric and electronic structure, superconductivity, magnetism, chemical reactivity, catalytic activity, and optical absorption—can vary dramatically, sometimes by several orders of magnitude, with changes in cluster size.

Fundamental questions therefore arise: How do clusters nucleate and grow? How do they transform structurally as atoms are added? At what cluster size does solid-like behavior emerge? Since atomic structure critically determines cluster properties, it is remarkable that these questions remain incompletely answered [8]. The inherent difficulties associated with theoretical modeling and experimental determination of cluster structures have been major obstacles. Consequently, much structural information has been inferred indirectly from other cluster properties, often leading to incomplete or ambiguous interpretations.

Studies of cluster yields induced by surface excitation also contribute to a deeper understanding of excitation mechanisms and sputtering processes. As cluster size increases, the emergence of collective physical phenomena—such as plasmon excitations, formation of conduction bands, superconductivity, superfluidity, phase transitions, and fission—can be observed. These many-body effects are characteristic of solids but absent in isolated atoms. Clusters exhibit distinctive properties that depend sensitively on their geometry, which strongly influences their stability. Determining the most stable cluster configurations is a nontrivial problem and varies among different materials. This issue is closely related to the phenomenon of cluster "magic numbers," which reflect enhanced stability at specific cluster sizes [9]. The formation of magic number sequences is intimately connected to cluster formation and growth mechanisms. It is therefore natural to expect that modeling cluster assembly and fusion processes can elucidate both magic number sequences and stable cluster isomers.

The present study provides systematic experimental data on cluster ion emission from several materials over a wide energy range and clarifies the influence of projectile type and surface conditions on cluster yield distributions. Some of the results have been presented earlier [11,12,26], but this paper presents a revised physical interpretation of the experimental data.

Although some experimental results were reported previously [26], the present work provides a unified physical interpretation of cluster emission mechanisms, including cascade overlap effects under molecular ion bombardment, correlated sputtering processes, and the distinct formation pathways of light and large clusters.

Experimental Methods

The experimental methods used to investigate cluster-ion formation during ion bombardment were developed and optimized for the present study [10,11,26].

Experimental studies of the emission of atomic clusters from surfaces when they are bombarded with different atomic particles under various conditions of invetsigation pose significant experimental challenges. In the above studies, special attention is paid to such units of the installations as sources of various primary ions, the method of forming an ion beam, systems for analyzing emitted particles, and an oil-free high-vacuum pumping system.

Cluster ion yields were measured using secondary ion mass spectrometry (SIMS) during the sputtering of solid surfaces by primary ions. Measurements of positive and negative cluster ion yields, $Yn^{\pm}$ under bombardment by N^+, O^+, N_2^+, O_2^+, and Ar^+ ions were performed for Al and GaAs targets in the primary ion energy range E_0 = 5–50 keV. The dependence of ion yields on oxygen pressure in the interaction chamber was also investigated. These experiments were carried out at the University of Salford (UK) using a SIMS setup combined with an energy analyzer [10].

Additional measurements of cluster ion yield from C, NaCl, Mg, Al, Si, S, and Ti surfaces bombarded by Ar^+ ions were performed in the energy range E_0=0.5–10 keV. The dependence of yields on the incidence angle α (measured from the surface normal) was studied using an ultrahigh-vacuum SIMS system developed at Ivane Javakhishvili Tbilisi State University [11,26].

A detailed description of both experimental methods and the corresponding setup parameters is presented earlier in our papers [10,11,26].

Results and Discussion

The yields of positive and negative cluster ions of different sizes

from the surfaces of C, NaCl, Mg, Al, Si, S, Ti, and GaAs were measured under bombardment by N^+, O^+, N_2^+, O_2^+ and Ar^+ ions in the primary ion energy range of 0.5–50 keV. Most of these results were reported previously in our publications [11,12,26], but this paper also presents new theoretical considerations.

The present work extends earlier experimental studies by introducing a unified interpretation based on cascade overlap effects, correlated sputtering, nonlinear energy-density scaling, and the distinction between light- and large-cluster emission mechanisms.

For metallic clusters, significant differences in size distributions have been reported depending on the experimental method, whereas for nonmetallic clusters, the ionization probability is relatively size-independent [3,5,9].

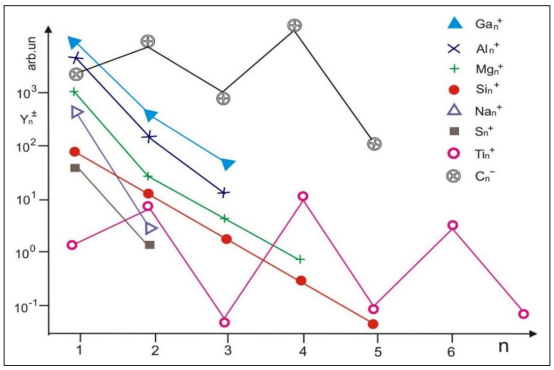

Figure 1: Cluster ion yields during Ar^+ bombardment of C, NaCl, Mg, Al, Si, S, Ti, and GaAs at Eo = 8 keV

In general, the cluster yield decreases strongly with increasing n; typically, the yield of clusters of size n + 1 is approximately one order of magnitude lower than that of clusters of size n. The relative cluster yield follows a power-law dependence on cluster size n [3,16,17,27].

$$Y(n)\alpha n^{-\delta} \tag{1}$$

The observed value of the exponent δ typically ranges between 2 and 15, in our case, for different solids, δ ranges from approximately 4 to 8, which likely depends on the electronic configuration of the emitted clusters [7]. Furthermore, the considerably large number of light (small) clusters is partially caused by the fragmentation of larger clusters.

Only two published models predict a power-law cluster yield distribution. The first is a shock wave-initiated process proposed by Bitensky and Parilis [23]. The second is the "equilibrium" model by Urbassek [8], which is applicable to sputtering by both singly and highly charged ions. In this model, a highly energized region of the surface undergoes a "liquid–gas" phase transition upon expanding into vacuum. In this model, clusters are assumed to be in equilibrium with each other and monatomic species. Reaching the critical point requires the kinetic energy of the target atoms to be high enough that chemical bonding loses its importance and the system becomes fluid. The equilibrium model predicts transitions from an exponential decay to a power-law decay as the phase transition occurs closer to the critical point [8]. The dependence of the cluster yield Y (n) on the cluster size n is given by:

$$Y(n) = Y_0 n^{-\delta} \exp\left[\frac{-\Delta G n - 4\pi n^2 / 3r^2\sigma}{kT}\right] \tag{2}$$

where ΔG is the difference in Gibbs free energies between the liquid and gas phases, k is the Boltzmann constant, T is the temperature of the energized region, Y0 is the sputter yield, r is the cluster radius, σ is the surface tension, and δ is the critical exponent [8]. At equilibrium, ΔG = 0, and at the critical point, the surface tension vanishes. Consequently, the predicted cluster size distributions at the critical point are very similar for both the equilibrium and shock-wave models. The equilibrium model is also capable of explaining variations in the power-law exponent over a limited range of conditions [24,25,27].

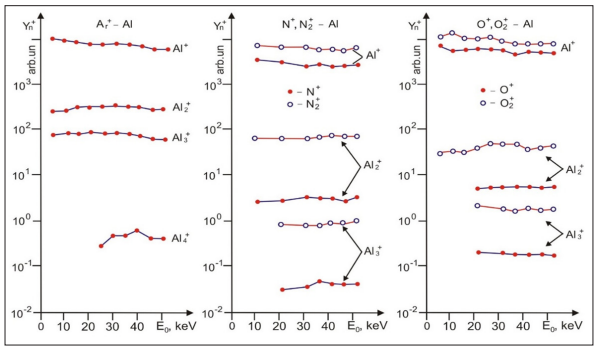

Figure 2: The yields of Aln+ ions during Ar+, O2+, N2+, O+, N+ - Al at Eo = 40 keV

Figure 2 shows that under molecular ion bombardment (e.g., N_2^+, O_2^+), the yield of Al_2^+ is approximately a factor of two higher than in the case of atomic ions (N^+, O^+). A similar tendency is observed for larger clusters.

These results cannot be explained within the framework of independent atom emission and instead indicate a correlated sputtering mechanism within the framework of Sigmund's approach. In Sigmund theory, an incident ion penetrates the target and initiates a series of binary collisions, producing a "collision cascade." The local energy deposition follows a Gaussian distribution around the ion trajectory. Sputtering of solids by energetic ions or recoil atoms is assumed to result from cascades of atomic collisions. The sputtering yield is calculated under the assumption of random slowing down in an infinite medium.

Within the formalism of Sigmund theory [27], the sputtering yield of monatomic species is proportional to the nuclear stopping power Sn(E), i.e.,

$$Y_i \alpha \frac{S_n(E)}{U_0} \tag{3}$$

However, cluster emission requires the simultaneous ejection of several neighboring atoms and therefore depends on higher-order correlations of the deposited energy density [27].

Assuming that emission occurs when the local energy density

exceeds a threshold value, the probability of emitting a cluster of n atoms can be expressed as a product of correlated emission probabilities. Under the approximation of short-range correlations, this leads to the scaling relation

$$Y_n \alpha \left(\frac{S_n(E)\Phi(\alpha)}{U_0} \right)^n \quad (4)$$

where Φ(α) describes the angular dependence of energy deposition. This nonlinear dependence implies that cluster yields increase more rapidly with deposited energy than monatomic yields, in agreement with the experimental observations.

A key factor governing the enhanced emission under molecular ion bombardment is the formation of **overlapping collision cascades.** Upon impact, molecular ions such as (N_2^+, O_2^+) dissociate into atomic constituents, each initiating a collision cascade in close spatial proximity. The resulting energy density distribution may be written as a superposition of two cascades [27],

$$\varepsilon(r)=\varepsilon_1 (r)+\varepsilon_2 (r-d) \quad (5)$$

where d is the separation between the cascade centers. The overlap of these cascades leads to an increase in the higher-order moments of the energy density, thereby enhancing the probability of correlated emission. As a consequence, the cluster yields under molecular ion bombardment can be expressed as

$$Y_n^{(mol)}=Y_n^{(atom)} C_n \quad (6)$$

where Cn>1 is a correlation factor that increases with cluster size. This may provide a plausible explanation for the experimentally observed increase in Al_2^+ and Al_3^+ yields.

The size dependence exhibits pronounced odd–even oscillations for Tin+ (n = 1, …,7) and Cn- (n = 1,5) clusters (Figure 1) [16,17]. Similar behavior has been reported by numerous authors for a variety of surfaces, including Agn+, Agn- and Cun- [18,19], and can be explained within the framework of the recombination model of cluster formation. For Ti, C, Ag, and Cu surfaces, emission of both positive and negative cluster ions is dominant. Small variations in the bombardment angle α (on the order of 10°) do not alter the overall structure of the cluster yield distributions for Ti however, the ratio of yields for clusters with even and odd n changes noticeably [11,26].

Differences in interatomic potentials and pairing interactions lead to significant variations in cluster structures, mass spectra, and magic number sequences. The origin of cluster magic numbers is rooted in quantum-mechanical effects. In this respect, light clusters are qualitatively similar to atomic nuclei, for which quantum shell effects play a decisive role in determining their properties.

A decrease in the ratio of single-atom to two-atom ion yields, Y12+ = Y1+/Y2+, was observed with an increase in the atomic number of the researched targets Na, Mg, Al, and Si (200, 60, 40, and 10, respectively). Such behavior of the ratio can be explained by the varying electronic configurations of the different emitted particles [20,26].

The yields Yn+(n = 1, 2, 3, 4) remain nearly constant over the investigated energy range, similar to the behavior observed for sputtered neutral Al atoms [20,21]. The yields Yn+(n = 1, 2, 3,) are lower for O^+–Al and N^+–Al bombardment than for O_2^+–Al and N_2^+–Al bombardment. This difference can be attributed to the deeper penetration of atomic O^+ and N^+ ions into the aluminum target, which leads to a reduction in cluster ion yields. The averaged maximum values of Yn in the saturation regime, together with the corresponding yield ratios Y2+/Y1+, Y3+/Y1+, and Y3+/Y2+, were determined experimentally. Similar behavior of the cluster yield dependence on the primary ion energy Eo was observed for Na, Mg, Si, S, Ga, and As clusters during bombardment of NaCl, Mg, Al, Si, S, and GaAs targets in the energy range E_0=0.5–50 keV, regardless of whether the bombarding ions were Ar^+, O_2^+, N_2^+, O^+, or N^+.

At higher primary ion energies, deviations from the simple cascade scaling behavior are expected due to the onset of **thermal spike effects.** In this regime, the energy density becomes sufficiently high to produce a transient, quasi-thermalized region in which atoms can be emitted collectively. The emission probability of clusters can then be described as a thermally activated process [27],

$$Y_n \alpha \exp\left(-\frac{E_b(\alpha)}{k_B T_s} \right) \quad (7)$$

where Ts is the spike temperature and Eb(n) ≈ nU0 – Δn is the effective binding energy of a cluster. This mechanism preferentially enhances the emission of larger clusters and may contribute to the observed behavior at higher energies.

Overall, the experimental results indicate that cluster ion formation in aluminum under ion bombardment is governed by a combination of **nonlinear cascade effects and local energy density enhancement,** with molecular ions playing a particularly important role due to cascade overlap [27]. The proposed description consistently accounts for:

- the higher yields of cluster ions under molecular ion bombardment,
- the stronger dependence of cluster yields on energy and angle of incidence,
- and the increasing contribution of collective (thermal spike) processes at higher energies.

The present results support a unified interpretation of cluster emission involving correlated sputtering, cascade overlap, and thermal-spike-assisted processes.

As evident from Figure 2, a significant reduction in cluster ion yields is observed for N^+–Al and O^+–Al bombardment—particularly in the case of N^+–Al with increasing cluster size. In addition, bombardment with oxygen ions leads to oxidation of the aluminum surface, which increases the probability of emission of secondary particles.

In the case of N_2^+–Al, the yield Y_1^+ is approximately twice as high as for N^+–Al. A similar trend appears for O_2^+–Al compared with O^+–Al. This behavior may be attributed to the dissociation of molecular ions (N_2^+, O_2^+) into atomic ions (N^+, O^+) during

their initial interaction with aluminum. Such dissociation could effectively lead to an approximately twofold increase in the Y_1^+ yield. For Y_2^+ and Y_3^+, however, interpretation of the experimental data remains uncertain, as it is difficult to separate the relative contributions of excitation, ionization, dissociation, and oxidation processes.

Owing to the larger mass, multi-electronic configuration, and more efficient momentum transfer of Ar^+ ions, their interaction with near-surface aluminum atoms is more effective, resulting in comparatively higher emission of cluster ions.

According to our previous investigations [22,27] the yields of various emitted species including single positive and negative ions, multicharged ions, cluster and molecular ions, as well as radiation during Ar^+ bombardment of aluminum at different oxygen pressures ($5 \times 10^{-10} - 1 \times 10^{-6}$ Torr) in the interaction chamber at a primary ion energy of $E_0 = 40$ keV [15,22,27]. An increase of two to three orders of magnitude in the yields of AlO^+ and AlO_2^+ cluster ions with increasing oxygen pressure indicates progressive oxidation of the aluminum surface. The yields of Al_2^+ and Al_3^+ cluster ions, as well as those of multicharged Al^{2+} and Al^{3+} ions, decrease by a factor of approximately 2–3 with increasing oxygen pressure Po2. In contrast, the behavior of photon yields associated with the radiative decay of excited aluminum atoms, (Al)* - (λ1) and ions, (Al^+) * - (λ2), differs markedly. The yield of excited neutral atoms increases significantly with increasing Po2, whereas the yield of excited ions decreases only slightly. The variations in emitted particle and radiation yields can be attributed to modifications of the surface electronic structure of aluminum induced by oxidation [22,26].

Analysis of the yields of various ions indicates a weak dependence on the incidence angle α within the range ($0^o - 45^o$). Numerous experimental studies of ion bombardment of solids have shown that, within this angular range, the yields of emitted ions and radiation remain nearly constant. The observed increase in the yields of Aln+ (n = 2, 3) cluster ions with increasing α can be attributed to a reduction in the average escape depth, which enhances the probability of cluster emission [20,22].

The dependence of cluster yields on the angle of incidence further supports this interpretation. As the angle α increases, the penetration depth of the primary ions decreases, resulting in a higher concentration of deposited energy in the near-surface region. Since cluster emission is governed by correlated processes, the yield scales as [27]:

$$Y_n(\alpha) \alpha \Phi(\alpha)^n \quad (8)$$

which implies a stronger angular dependence for clusters than for monatomic species. This is consistent with the observed increase of Al_2^+ and Al_3^+ yields with increasing angle of incidence.

The yields of Al^+ ions, as well as molecular species such as AlH^+, AlO^+, and $AlOH^+$, increase by approximately a factor of two when the projectile is changed from N^+ to N_2^+ and from O^+ to O_2^+, in contrast to the behavior of Al_2^+ and Al_3^+ ions. The yield of Al_2O^+ increases by more than one order of magnitude when atomic projectiles (N^+, O^+) are replaced by molecular ions (N_2^+, O_2^+). A high ion yield, particularly for Al_3^+, is also observed in the case of Ar^+–Al bombardment. At the high bombardment energies of N_2^+ and O_2^+ ions (tens of keV), it is reasonable to assume that dissociation of the molecular ions occurs during the initial collision step, resulting in effectively doubled intensities (ion + atom) and a redistribution of the primary energy E0 between the fragments [16,17,22,28].

Following cluster emission, several complex processes—such as fragmentation, ionization, and de-excitation—take place, complicating the identification of the underlying cluster formation mechanisms [8]. It is therefore reasonable to assume that the mechanisms governing the emission of light clusters with $n \leq 10$ differ from those responsible for the emission of larger clusters ($n \geq 10$).

Developing a unified physical picture of cluster emission during surface sputtering bridges the gap between rapid, localized collision cascades and slower, collective macroscopic phenomena.

The emission of clusters cannot be explained by a single temporal event. Instead, molecular dynamics simulations and experimental yields point to a timeline split between an early "collisional" phase and a delayed "thermal/hydrodynamic" phase [3].

The Collisional Phase: Small Cluster Emission

Within the first picosecond of ion impact, energy transfer creates a highly directional linear collision cascade.

- **Mechanism:** Small clusters ($n < 10$) are emitted by collective motion when an energetic sub-cascade intersects the surface layer.
- **Composition:** These clusters are almost exclusively composed of atoms that were nearest neighbors on the original lattice surface.
- **Yield:** The relative yield decays rapidly (often modeled statistically via an exponentially decaying or steep power-law distribution) as cluster size increases.

The Thermal Phase: Large Cluster Emission

The emission of massive clusters ($n > 10$, sometimes exceeding hundreds of atoms) requires an entirely different physical model, as they are ejected much later—typically 5–10 ps after impact.

- **Mechanism:** When the impinging ion deposits its energy locally in a small subsurface volume, it generates a dense "thermal spike." The extreme temperature and pressure induce localized melting, and the resulting hydrodynamic shock wave ablates the surface, ejecting large fragments [3].
- **Composition:** Unlike small clusters, these large fragments consist of atoms mixed from various subsurface layers, reflecting the rapid diffusion that occurs in the melt zone prior to ejection.

Calculations reported in [3,4,7,29] show that sputtering in the form of atoms occurs within several hundred femtoseconds after ion impact, while the emission of light clusters takes place within the first picosecond; detection of these species occurs

tens of microseconds after emission. Detailed analysis indicates that most nascent excited clusters possess a very high degree of internal (vibrational) excitation, with an average excitation energy of approximately 1 eV per atom. Owing to the picosecond timescale of the fragmentation processes, the clusters detected experimentally correspond primarily to the final metastable end products.

According to [3], Al_2^+ clusters formed from adjacent surface atoms and Al_3^+ clusters are emitted within the first picosecond after bombardment; consequently, simultaneous ion–atom collisions associated with molecular projectiles play an important role [7,29]. In addition, partial transfer of internal excitation energy into the electronic subsystem occurs, and exchange interactions between the surface electronic structure and the electronic states of the emitted complex ultimately determine the final state of the cluster.

According to Molecular Dynamics (MD) computer simulations [3], the sputtered flux consists predominantly of atomic particles originating from the first atomic layer (92%), with 5.1% coming from the second layer, 1.3% from the third layer, and 1.4% from deeper surface layers. Approximately 60–70% of all clusters with $n > 3$ originate exclusively from first-layer atoms [3].

As the surface evolves during sputtering, so-called "ragged connections" between atoms may appear. These configurations are energetically unfavorable; as the system approaches equilibrium, additional constraints develop between atoms, leading to the formation of bonded pairs (dimers). The main mechanism of cluster emission from metals discussed in [3,7] is the so-called double-collision mechanism. This mechanism is based on the fact that, for metals and semiconductors, the dissociation energy of a dimer is typically smaller than the surface binding (sublimation) energy. Consequently, if sufficient center-of-mass energy is transferred to a dimer, its internal energy is usually so high that it cannot survive intact during emission from the solid. Within the double-collision mechanism, dimers and larger clusters are formed from independently ejected atoms when they are emitted sufficiently close in time and space and when their relative kinetic energies are lower than the binding energy of the corresponding dimer or cluster [1,6].

Cluster formation during ion sputtering of solid surfaces is a complex dynamic process that has been interpreted within several complementary theoretical approaches [3,5,9,27]. In the recombination (agglomeration) model, clusters are formed outside the surface from independently ejected atoms whose relative kinetic energies are smaller than their binding energies. This mechanism effectively explains the formation of small clusters during low- and medium-energy ion bombardment. In the direct-emission model, neighboring atoms are emitted collectively as an already bonded fragment detached intact from the surface. Such processes become important for large molecular structures and strongly bound surface regions. Under conditions of high local energy density, thermal spikes and shock-wave processes may additionally develop, leading to delayed emission of large, highly excited clusters that can subsequently undergo fragmentation after sputtering.

Instead of linear cascades, a so-called thermal spike is created — a microscopic local area of the surface where energy is instantly converted into heat, and the material locally approaches a transient molten state. The high pressure and shock waves generated during this state cause the ejection of a large volume of material. Such processes may contribute significantly to the emission of large clusters (where the number of atoms is $n > 10$). The ejected clusters are often in a state of high internal excitation (vibrational/rotational excitation) and may undergo secondary fragmentation (unimolecular decomposition) after emission.

The dominance of a particular emission mechanism depends strongly on the mass, energy, and incidence angle of the projectile ions, as well as on the surface binding energy and structural properties of the target material.

The proposed interpretation suggests that light clusters are predominantly associated with collision-cascade collective motion, whereas large clusters originate mainly from delayed spike-related emission processes. Molecular-ion bombardment enhances cluster formation through overlapping cascades, while fragmentation processes contribute significantly to the observed size distributions.

Conclusions

The present results indicate that cluster emission under ion bombardment is governed by different physical mechanisms depending on cluster size. Small clusters ($n < 10$) are primarily formed during the early collision-cascade stage within the first picosecond after impact, whereas the emission of large clusters ($n > 10$) is associated with delayed thermal-spike processes.

Molecular ion bombardment (N_2^+, O_2^+) produces enhanced yields of Al_2^+ and Al_3^+ clusters compared with atomic projectiles, which is attributed to overlapping collision cascades and correlated emission processes. The observed differences between atomic and molecular bombardment may also involve the formation and fragmentation of excited cluster states.

Overall, the proposed interpretation consistently explains the experimental cluster-yield distributions and highlights the important role of cascade overlap, local energy-density enhancement, and fragmentation effects in cluster formation during sputtering.

Acknowledgment

The author sincerely thanks all colleagues and collaborators who contributed to discussions and experimental work related to this study.

Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit Authorship Contribution Statement

George G. Meskhi: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing. The author is the sole contributor to this work and prepared the article independently.

Data Availability
Data will be made available on request.

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