Nuclear Instruments and Methods in Physics Research B 303 (2013) 136–141

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Sputtering of Al nanoclusters by 1–13 keV monatomic or polyatomic ions studied by Molecular Dynamics simulations

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ARTICLE INFO

Article history:
Received 12 July 2012
Received in revised form 17 December 2012
Accepted 10 January 2013
Available online 18 January 2013

Keywords:
Molecular Dynamics
Nanoclusters
Sputtering
Desorption

ABSTRACT

Molecular Dynamics (MD) simulations were employed to study sputtering of freestanding and supported spherical Al nanoclusters with 2–10 nm diameters under bombardment by Al_1 and Al_{13} projectiles with energies of 1–13 keV at normal and oblique incidence. Both monatomic and clustered yields of secondary emission are found to be larger than those for (1 1 1) flat surface of the bulk Al (at equal irradiation conditions). In some events, target nanocluster receives a backward momentum and therefore its major part (more than 1/2 of the mass) is ejected due to produced secondary emission mainly towards the substrate direction. This "recoil effect" is found more pronounced under the impact of cluster projectiles and its probability decreases with increase of the target cluster size. A restricted number of MD simulations were performed to verify whether this "recoil effect" is strong enough to desorb a 4 nm Al nanocluster off an Al (1 1 1) substrate. Desorption was observed under oblique Al_{13} impact within the impact parameter range of 0.6–0.9.

1. Introduction

Nowadays there is an increased interest in studying nanomaterials sputtering due to the progressive development of nanotechnologies. In fact a new line in investigation of sputtering is formed, in frame of which secondary emission under ion bombardment of nanoclusters (and nanostructures) is studied [1]. Because of finite-size effects, such as high curvature of a surface and a large surface-to-volume ratio, studying of sputtering and atomic collision cascades in such systems is of fundamental interest. It was shown by various research groups [2–6] that increase in the sputtering yield of a nanocluster in comparison with a flat surface (under equal irradiation conditions) is typical effect. Practical interest for such kind of research is related, in particular, to recent development of methods of secondary ion mass spectrometry (SIMS) for studying and analyzing nano-dispersed and biological materials [7–11]. Increasing of the SIMS efficiency is an indubitable motivation for studying sputtering of nanoparticles too. For instance, as it was shown in [7], efficiency of the Time-of-Flight SIMS method for molecular solids is dramatically enhanced by first coating the sample with metal nanoparticles. Moreover, phenomenon of desorption of deposited on a substrate nanoparticles under ion irradiation is of particular interest because it can be a basis for development of a new generation of nanoparticle beam sources [12]. Currently phenomena of sputtering and desorption of nano-structured materials remain insufficiently explored. As it is impossible to obtain "free standing" nanoclusters in an experiment, preliminary deposited on a substrate clusters are used in practice. In such cases nanoclusters form either a continuous film, or so-called nano-dispersed discrete structure (when surface density of deposited nanoclusters is low and they do not overlap with each other). For the first time sputtering of a continuous nanocluster film was studied in [13], where increase in sputtering yield as compared with polycrystalline material was found. Furthermore, ion bombardment of nano-dispersed targets that contained isolated gold nanoclusters was experimentally studied in [8], [14–19]. Desorption of "whole" nanoclusters was first experimentally observed by irradiation of nano-dispersed targets by heavy fission fragments [14] with energy higher than 14 MeV (i.e. electronic stopping dominates), at the same time cluster ejection yield reached ~10–500%. Secondary cluster emission was also discovered at lower projectile energies, when nuclear stopping power dominates, however, under such conditions secondary emission yields were lower [20,21]. There is evidence that the use of cluster ion beams should increase efficiency of desorption under low projectile energies [22–24]. In particular, in experiments [24,25] desorption of gold nanoclusters (with 6 nm mean size) from graphite substrate was observed under bombardment by beams of 38 keV Au_1 ions and 72 keV Au_{400} clusters directed at 45° to the substrate. Value of desorbed nanocluster yield (rescaled per one impact and normalized on probability of direct hit) came to ~1–5% under irradiation by Au_1 and ~60% under irradiation by Au_{400}.

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0168-583X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.nimb.2013.01.028

Phenomenon of desorption of a cluster, preliminary deposited on a substrate, was also studied using atomistic numerical modeling. Thus, in [26,27] desorption of gold nanocluster located on a golden substrate was explored. It was shown that origin of an intense heat spike in the substrate can lead to desorption of the deposited nanocluster by intense flux of "evaporated" matter. Another mechanism was found in [28,29] where desorption of a carbon nanocluster adsorbed on a graphite substrate was studied. It was found that massive projectile cluster can cause an acoustic wave with energy high enough to remove deposited molecules and clusters (so-called "trampoline effect"). It is important to notice that all above-mentioned mechanisms of desorption are related to "indirect impact" (when projectile hits the substrate without touching the deposited cluster). The possibility in principle of desorption a nanocluster by "direct impact" (i.e. under immediate collision of a projectile with a target cluster) due to the "recoil effect" was firstly demonstrated in [5,6,24,25]. The main point of this effect is that peripheral impact of the projectile in the lateral part of the target can cause intense secondary emission of atoms of the nanocluster towards the substrate giving the nanoparticle an upward momentum, away from the substrate [3,5]. Another cause of desorption is the so-called "popcorn mechanism". This mechanism can be realized in situations when the projectile energizes the nanoparticle without destroying it, such that it can be considered to be suddenly heated and thus may be desorbed from the substrate by a combination of two following effects: (1) – It is energetically more favorable for the nanoparticle to have rounded form. While acquiring its rounded form, the center-of-mass of the nanoparticle will move away from the surface and imparted momentum can lead to desorption; (2) – Sudden increase of the nanoparticle temperature will lead to large compressive pressure. If this pressure is particularly high at the substrate-nanoparticle interface, it will accelerate the nanoparticle away from the substrate, leading to desorption. However, it should be mentioned that the "popcorn mechanism" is effective only if nanoparticles have nonspherical overall shapes. In [30] computer simulation of desorption of hemispherical Au nanoparticles from a graphite substrate was made, mechanism related with pressure increase was mainly observed. Similar mechanism was found in experiments where nanoparticles were desorbed from the graphite substrate using laser beam [31]. Analogous process was described in works devoted to desorption of bio-molecules off the surface [32], where the term "popcorn mechanism" was firstly proposed. Specific mechanisms responsible for desorption of large bio-molecules under low-energy cluster bombardment were discussed in [33]. At least two important mechanisms were detected: so-called "spring" (in which the molecule is compressed under hit on the rigid substrate and then reacts like a spring gaining enough translational energy to desorbs) and "washing" (in which the molecules are washed away by the projectile constituents and entrained by their flux). All above-listed mechanisms can be responsible for desorption of nanoparticles from a substrate under irradiation, but actual mechanism which appears in particular experiment strongly depends on specific irradiation conditions, structure and size of nanoparticles, substrates and other factors. Thus, it is impossible to formulate universal laws of desorption.

In the present work we study the sputtering of Al_N spherical nanoclusters with diameter of (2–10) nm under bombardment by monatomic Al_1 ions (with energies of 1 and 13 keV) and polyatomic Al_{13} clusters (with fixed initial energy per atom – 1 keV/atom) using classical Molecular Dynamics simulation. Furthermore, the possibility of desorption of Al_{1985} isolated cluster (4 nm diameter) deposited on the flat Al (1 1 1) substrate under the same irradiation conditions was studied. The aim of this research is systematic study of sputtering characteristics vs. target particle sizes and irradiation conditions. A special attention in this study is paid to analysis of secondary emission of clustered particles and ejection mechanisms of large clusters which can lead to desorption.

2. Simulation technique

Numerical simulations are performed within the framework of classical Molecular Dynamics (MD) method [34,35], which allows tracing individual trajectories of each particle of considered system by means of Newton's motion equations solving. Details of used method are described in [5,6,27,36,37] so we will explain only basic features. MD code utilizes a many-body interatomic potential which is based on the Second Moment Approximation of the Tight Binding (SMA TB) model [38] combined with Ziegler–Biersack-Littmark (ZBL) potential [39] at short distances for correct treatment of atomic collisions with high energies. As it was shown in [36,37] using this cohesive model the Al self-sputtering yield can

Table 1
Summary of secondary emission characteristics under various irradiation conditions.

Projectile	E, keV/atom	Target nanocluster Al_N		R_p/D	K_{tm}	Emission of large particles					
						P_d, %		$\langle N_{sp\_cl}\rangle$		$\langle E_{sp\_cl}\rangle$, eV	
		N	D, nm			$\theta = 0°$	$\theta = 45°$	$\theta = 0°$	$\theta = 45°$	$\theta = 0°$	$\theta = 45°$
Al_1	1	249	2	1.25	0.93	46	45	211	217	0.76	0.77
		1985	4	0.63	0.74	0	17	–	1955	–	0.36
		6819	6	0.42	0.60	0	0	–	–	–	–
		16187	8	0.31	0.53	0	0	–	–	–	–
		31389	10	0.25	0.49	0	0	–	–	–	–
Al_1	13	249	2	10.9	1.00	24	22	221	214	0.57	0.48
		1985	4	5.4	0.99	11	13	1947	1973	0.40	0.32
		6819	6	3.6	1.00	2	6	6798	6792	0.21	0.24
		16187	8	2.7	0.99	1	7	16144	16163	0.32	0.33
		31389	10	2.2	0.97	1	0	31329	–	0.21	–
Al_{13}	1	249	2	1.25	1.00	13	14	197	199	1.29	1.46
		1985	4	0.63	0.95	18	23	1449	1647	7	13
		6819	6	0.42	0.83	30	35	5244	5348	18	22
		16187	8	0.31	0.61	17	53	10635	13431	28	31
		31389	10	0.25	0.52	0	22	–	30239	–	20

Symbols: E – initial projectile energy per atom (keV/atom), N – number of atoms in target cluster; D – cluster diameter (nm); R_p/D – projectile range to target diameter ratio; K_{tm} – coefficient of transmitting of projectile atoms; θ – angle of incidence; P_d – probability of target cluster desorption(%); $\langle N_{sp\_cl}\rangle$ – mean size of sputtered "large" particles (i.e. $N > N_0/2$); $\langle E_{sp\_cl}\rangle$ – mean translational kinetic energy of sputtered "large" particles (eV).