Surface Modification by 1 keV Ar Ion: Molecular Dynamics Study of Ar^+-Ni(100) Collision System

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Abstract – Ar+Ni(100) collision system was investigated by using isoenergic Molecular Dynamics (MD) simulations. We have focused on the sputtering process upon ion-impact and surface damage. Our earlier sequential MD simulation program was first converted into a parallel code [1], and then, it was used to study threshold energy region of the sputtering process on the Ni(100). Next, we have used this code with an effective and favorable algorithm to mimic a real 1 keV ion impact on Ni(100) experiment [2]. The Ni(100) slab is formed by 63700 atoms. In order to preserve the total energy in the simulation at this collision energy a small time-step (0.1 fs) is used. The total observation time is about 2.25 ps. Results were found to be in good agreement with the experiment [2].

1. Introduction

In this work we will examine such a collision system and try to understand the mechanism behind the onset of sputtering. Particularly we will discuss Ar-Ni(100) system because of the large discrepancy between the experimental [3] and theoretical [4] results.

Since our goal is to simulate very high bombarding energy regions, one has to optimize and parallelize the algorithm. Therefore, here, we discuss in a step-wise manner parallelization of our sequential code.

We should here mention that in general large scale MD works in the literature (Refs. 5–8) have focused on plastic deformation and large scale dislocations. Therefore, optimum Domain Decomposition (DD) algorithms are used, which suits quite well into the physics of the simulations, in those studies. On the other hand, our DD algorithm has been developed for the ion-surface collision system, ion's impact energy is the key factor to determine the size of the system, and the primary objective is to be able to do a full simulation of the ion-surface collisions rather than maximizing the system size with the available hardware at hand. Because of this we have considered many-body interaction potential for the surface, which describes quite well the Ni crystal instead of pairwise additive potential. It is obvious that the run time for each MD step must be decreased, and the system size must be increased. For these aims, we have made use of some optimization and parallelization techniques which are namely dynamic memory allocation (DMA), optimal pair listing (OPL), parallelization via message passing paradigm (MPP), and single instruction multiple data (SIMD) approach [9].

It is feasible to share the atoms to processors as N_{atom}/N_p (DD). Here N_p is the number of processors. The load balancing is achieved since every processor has equal amount of atoms. The overwhelming part of the total computation time in any MD simulation is spent for the calculations of the potential energy surface (PES) and the forces.

At low energies (below 100 eV), there are some theoretical and experimental studies, however, theory and experiment on the Ar-Ni(100) collision system are quite scarce. In the literature, only a few low energy MD studies of sputtering process for the Ar-Ni(100) system [4,10,11] exist. Most of the low energy studies [12–19] were carried on amorphous and closed packed aluminum, copper, and nickel (Al, Cu, Ni) surfaces bombarded by Ar^+ and/or Cu^+, Al^+, Ni^+ ions, respectively. In the present work we have chosen this Ar-Ni(100) system since the threshold region of the sputtering event is not well known, and its energy dependence has not been studied within the range of 10–150 eV.

In this work, the sequential code is parallelized as a further development by using message passing paradigm and master-slave approach. We have made use of PVM for the communications between the tasks of the parallel program. Performance tests of this parallelized code were made using different size of the slabs. Finally, the code was used for the size of 13248-atom slab (79 E×79 E×19 E). The ion impact energy was in the range of 10–150 eV, and the sputtering yields were calculated. Each of the impacts was followed up to 4 ps for the threshold energy regions. After that, 63700-atom slab was used for the 1 keV Ar^+ ion. The time-step was set as 0.1 fs after the test runs, and the total observation time was 2.25 ps. The behaviors of the ion and the sputtered Ni atoms, and the yields were investigated.

2. Computational Procedure

We have achieved to handle 1.5 millions of atoms with our developed parallel algorithm. However we are unable to do a full simulation of this size of the collision system with the present hardware. Results of the sequential and the parallel runs (Linux (Debian 2.4.20) with a compiler option −O2 optimization level is used) are compared and assured that they are the same both in numerical accuracy and in physical aspects. The code is tested in a distributed memory system consisting of a cluster of 8 PC's.

The crystal surface was modeled by Voter-Chen version [20] of embedded atom potential (EAM) [21], and its short range repulsive part was improved to simulate such a high impact energy in this work. The EAM formalism is given as,

$$V = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(r_{ij}) \right], \qquad (1)$$

where $F_i(\bar{\rho}_i)$ is the energy required to embed atom i into the background electron density at site i, and $\phi_{ij}(r_{ij})$ is the core-core pair interaction between the atoms i and j seperated by the distance of r_{ij} (see for details Ref. 20). Furthermore, the interaction between the projectile and the surface was modeled by using Ziegler-Biersack-Littmark (ZBL) screened Coulomb type potential [22]. A coulomb type potential for the projectile-slab interaction is given as,

$$V(r) = \frac{Z_1 Z_2}{r} \Phi(r/a), \qquad (2)$$

where screening-function $\Phi(r/a)$ is approximated by

$$\Phi\left(\frac{r}{a}\right) = \sum_{i=1}^{n} c_i \exp\left(-d_i \frac{r}{a}\right),$$

$$\sum_{i=1}^{n} c_i = \Phi(0) = 1. \qquad (3)$$

Z_1 and Z_2 are the atomic numbers of the atoms involved, a is the screening length in units of Å that has the form for the ZBL potential

$$a = 0.4685023\left(Z_1^{0.23} + Z_2^{0.23}\right)^{-1} \qquad (4)$$

as described Firsov [22] (n=4, c_1=0.028171, c_2=0.28022, c_3=0.50986, c_4=0.18175, d_1=0.20162, d_2=0.40290, d_3=0.94229, d_4=3.1998 in this reference). The ZBL potential is repulsive and practically goes to zero near 3.5 Å. The crystal, consists of 63700 atoms, has dimensions of 122 Å×122 Å×44 Å, and the atoms in the bottom layer (2450 atoms) are held fixed at their equilibrium positions during the simulations. This size of the slab used in this study is the largest in the literature at this ion impact energy. All the physical quantities such as; sputtering yield, probability of the ion remaining below the surface, angular distributions of the sputtered crystal atoms and reflected ions were extracted from 820 different ion collisions for the 1 keV ion impact. Ion impacts have covered one fourth of a surface unit cell at the center of the surface as seen in Fig. 1.

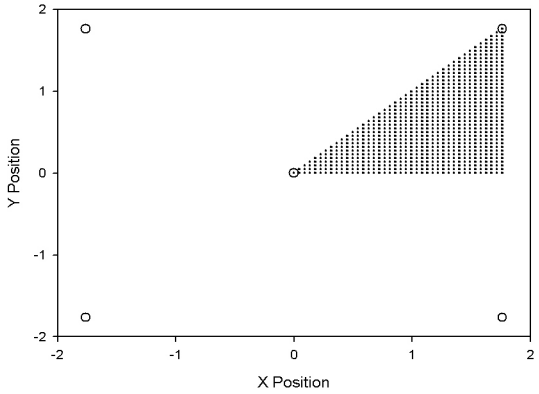

Fig. 1. The area covered by the ion impacts on Ni(100) surface

At the beginning of the simulation, the ion is placed at a distance of 9.5 Å above the surface, and it moves towards the crystal along the surface normal. Dynamics of all the atoms are followed by Hamilton's equations of motion, and solved for all the atoms in our system using Hamming's modified 4th order variable step size predictor-corrector propagator.

3. Results and discussion

Our approach in the parallelization of the system does distribute almost all parts of the MD simulation evenly (same instructions with different data for all the processors, SIMD), and keeps the communication as minimum as possible to avoid higher cost of the inter-node communication time. This significantly reduces the communication requirements and enables much better scaling to the larger number of processors (see Fig. 2). As seen, this scaling behaves nearly linear without depending on the system size since the amount of the data to be transferred is kept constant.

Results of Ref. 4 (filled circles in Fig. 3) have large discrepancy with the other theoretical and experimental studies as seen due to the inadequate description of the Ni-Ni and Ar-Ni interaction potentials. The sputtering yield of this collision system (Fig. 3) is calculated from N_s/N_c. Here N_s and N_c denote the total number of sputtered nickel atoms and the total number of collisions, respectively.

However, this Morse type potential did not work well towards the threshold energy. Furthermore, because of the ion's larger penetration depths, after the initial ion impact, the secondary Ar-Ni collisions dominate the sputtering dynamics [11]. In our present work we consider, instead of Morse type, screened Coulomb type, the ZBL, potential [16] for the Ar-Ni interaction, and the slab is mimicked by the same EAM. In Ref. 10, for the Ar-Ni part, four screened Coulomb type potentials were considered, however the number of collisions was small, and the slab was

much smaller than that of the present work. Agreement with the experimental values at low collision energy range (30 eV and above) was not so good.

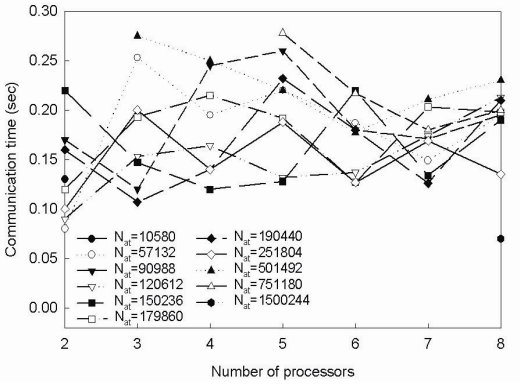

Fig. 2. Communication time per MD step (s) versus number of processor for different number of atoms

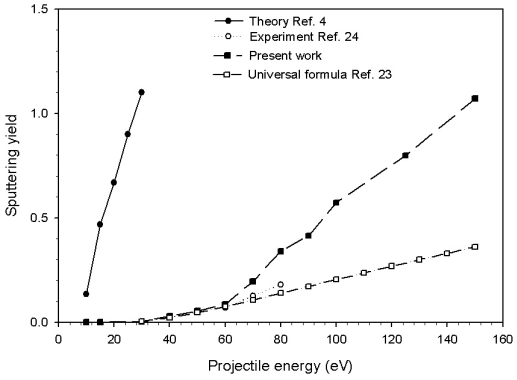

Fig. 3. Yields

We have observed that dynamics of the sputtering event near threshold energy is dominated by the Ni-Ni collisions after the initial normal incidence ion impact since only small amount of penetrations (less than 1 Angstrom) are observed up to 60 eV with the screened Coulomb type PES. Therefore, the sputtering process observed in this work is different than that of Ref. 11. The sputtering yield is much smaller near the threshold impact energy. Therefore one needs to consider larger number of ion impacts to reduce the uncertainty on the sputtering yield, and better description of the slab for this energy region. So, in this work we have improved the model used in Refs. 10 and 11 as follows. The Ni(100) crystal is mimicked by 13248 atoms whereas in Ref. 10 the slab was formed by only 867 atoms. Here, these atoms are equally divided between the two computing nodes of our clusters. Edge effects are negligibly small with the present dimensions of 79 Å×79 Å×19 Å the slab. The atoms at the bottom layer (1104 atoms) are kept fixed at their equilibrium positions during the simulations. Temperature of the nickel crystal is increased in a step-wise manner from 0 K to near 300 K. As a result, surface relaxation has occurred during this heating process. In order to mimic realistic ion-surface collision event, we have created 100 different sets of phase space coordinates of the slab, and selected randomly each of these phase space coordinates for every collision event (these phase space coordinates have been recorded in a run at 300 K, and the spacing between the sets is about 0.4 ps). Physical quantities have been extracted from 900 ion-surface collisions at each of the impact energies. Convergence of the sputtering yield is good as seen in Fig. 1. The ion energy <70 eV our yields (filled squares) are in good agreement (reproduces the variation of the yield with the Ar energy) compared to the empirical formula of Yamamura et al. [23], (open squares in Fig. 3), and to the experimental work (open circles) [3]. Up to this impact energy (60 eV) only the Ni-Ni collisions, after the initial Ar impact, are effective in the sputtering process due to very small amount of penetration of the ions. On the other hand in the case of some penetrations (above 1 Angstrom) of the Ar (above 60 eV), sputtering of the surface atom which is the result of the secondary Ar-Ni collision after the initial ion impact is more efficient process (i.e., as Ar returns and moves back towards the vacuum, it may kick a Ni atom from behind and cause sputtering or a surface damage). Therefore the slope is increased in the yield (behavior is also nearly linear) above 60 eV. Increasing in the slop of the empirical formula is not observed, however, there is a small increase in the slop of the experimental values (above 60 eV). As seen the threshold energy is near 30 eV (only two sputtering events out of 900 collisions are observed at this energy) for the normal ion incidence (at 10 and 20 eV of the impact energies we haven't observed any sputtering), and for the experiment [24] and universal formula [23], as well. So the results are all in good agreement. The results of Ref. 4 however, are too different due to the above mentioned reasons. We should also mention here that our goal is not to reproduce exactly the experimental sputtering yields, and note that the measurements carried out by Stuart and Wehner [24] were on polycrystals at very high bombardment fluencies. Therefore the target was damaged and saturated with implanted beam atoms. However, this is the only experiment available in the literature on this collision system at low energy. In addition we should also mention that Laegreid and Wehner [3] did an experiment on Ar^+ incident on polycrystalline gold, and their yields are 20 % smaller than those of Colligon and Bramhen [25] for the same Ar/gold system. There is, thus, some variability in the experimental data, and in Ref. 24 no error bars were reported for the Ar-Ni-surface experimental data.

In the collision experiment with 63700 atoms at 1keV ion impact energy, the sputtering yield is calculated as about 3.2 from 820 different ion collision (they have different surface phase and impact points) that is in good agreement with the experimental va-

lue of 2.6 [2]. Universal formula gives approximately 1.7 [23]. Distribution of sputtered Ni atoms in the x–y plane at the asymptotic region mimics almost the surface unit cell. The sputtering distribution has a maximum at near angle of 45° (angle with the z-axis). The back scattered Ar^+ ions have narrow angular distribution (within a narrow cone around the z-axis). In this 1 keV experiment the sputtering is observed only from the first four layers of the Ni(100). The majority of the sputtered Ni atoms are from the first layer (2554 Ni atoms), and the sputtering from the second, third and the fourth layers are 219, 16 and 4 atoms, respectively. Among 820 ion impacts the back scattered Ar^+ ions are about 43 %. About 49 % of the impacts the ions are remained in the slab. And the rest of the ions have passed through the slab.

4. Summary

Sputtering yields, and energy distributions of the scattered Ar, and sputtered Ni atoms for Ar-Ni(100) collision system have been calculated from 10 to 150 eV and at 1keV of the impact energies. Our calculated yields are compared to the available experimental and theoretical results. The agreements with the experiment look good. In this low energy regime the penetration depths of the Ar are nearly zero or positive, therefore, the Ni-Ni collisions, after the initial Ar-Ni collision, become the only possible channels for the sputtering. This mechanism involves several collisions, and mostly creates surface damages. The slope of the yield increases above 60 eV since there are some penetrations into the surface from some regions of the surface unit cell. Therefore after the initial ion impact, the secondary Ar-Ni collisions also contribute to the sputtering in addition to the Ni-Ni processes. However the damage is highly localized. On the other hand, at 1 keV ion impact energy collision cascade is formed, and the surface damage propagates more into the slab. This shows that the sputtering process is sensitive to the ion's impact energy. Since the experiment on the Ar-Ni-surface system is quite old, it is desirable to repeat this experiment with the present high technology, and measure all the possible physical quantities. This way full comparison could be done with the experimental results. This is important for the development of a good potential energy surface as well.

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