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Erosion of Ag surface by continuous irradiation with slow, large Ar clusters

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ABSTRACT

Molecular dynamics computer simulations are employed to probe processes taking place during continuous irradiation of Ag(1 1 1) surface by keV Ar_{872} projectiles. Surface modification, the total sputtering yield, and the angular distributions of ejected species are calculated at fluences ranging from 0 up to $\sim 6 \times 10^{13}$ impacts/cm^2. It has been shown that two trends can be identified in the development of surface roughness. At the beginning surface roughness increases fast. This fast increase terminates around 1×10^{13} impacts/cm^2 and is followed by a slow increase that finally saturates. The effect of the surface roughness on the sputtering yield depends on the impact angle. At normal incidence the sputtering yield is rather insensitive to the development of the surface topography. Modification of the surface morphology has, however, a significant influence on the total sputtering yield at large impact angles. Both the shape of the sputtering yield dependence on the impact angle and the angular spectra of ejected particles are sensitive to the surface roughness.

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1. Introduction

The gas cluster ion beam process, which utilizes a large aggregation of atoms or molecules as an ion beam source, has been shown to have great potential in nano-scale surface modification processes such as shallow implantation, surface smoothing, high-speed etching and thin film formation [1,2]. Substrate defects induced by colossal clusters have been investigated both experimentally [1,2] and theoretically [3–7]. However, almost all theoretical cluster studies were performed on flat surfaces. In other words, the investigated impacts were independent and reflected the experimental condition of zero fluence. Performing simulations of high fluence experiments, however, is computationally challenging. Only a few attempts have been done to date to trace accumulated effects by multiple impacts of cluster projectiles or to probe processes stimulated by single impacts at artificially modified surfaces. Moseler et al. investigated the smoothing of thin film growth due to an energetic cluster impact on "tilted" areas of the film [8]. Aoki et al. utilized a Si sample covered with artificially placed geometrical blocks [7] or a sample with predefined, sine wave, surface features [9] to examine the effects that the surface roughness on a smoothing process by Ar clusters of hundreds to thousands of atoms. Only very recently, new studies investigating evolution of surface roughness during continuous cluster bombardment have been published [10–13]. These studies have shown, for instance, that the final roughness of bombarded surface is correlated with the vertical dimensions of a crater formed by a single impact [12].

The main goal of this study is to apply a procedure that allow the investigation of the effects stimulated by continuous bombardment [10] to trace evolution of surface topography induced by impacts of 20 and 40 keV Ar_{872} cluster projectile directed at 0° and 70° relative to the surface normal, and to check if, and to what extent, the development of the surface topography can influence such experimental characteristics as the total sputtering yield and angular distributions of sputtered particles.

2. Model

Details of MD computer simulations as well as the potential parameters used to model cluster bombardment are described elsewhere [14,15]. Developed "divide and conquer" scheme for performing several impacts simultaneously, while preserving the time dependence of the impact sequence is applied to model sample evolution induced by continuous cluster irradiation [10,11]. The main sample used in the current study consists of a Ag{1 1 1} crystal, measuring 53×53 nm in width and 27 nm in depth. The sample contains approximately 4.5 million atoms. The single impact is, however, performed on smaller local sub-sample, which has been cut from the main sample. The local sample size depends on the size of the projectile and its initial kinetic energy. For 20 and 40 keV Ar_{872} projectiles, it has been found that the sample should be a combination of a cylinder with a radius of 11 nm

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and a height of 10 nm measured from the bottom of the deepest valley, capped at the bottom with a hemisphere of the same radius. The shape and size of the samples were chosen based on visual observations of the shape and size of collision cascades stimulated by impacts of Ar_{872} projectiles with various energies, directed normally to the Ag{1 1 1} surface. Each single impact was followed up to 36 ps. This amount of time was sufficient to allow collision process to occur and then the sample to equilibrate. Rigid and stochastic regions measuring 0.7 and 2.0 nm, respectively, were used on the bottom as well as cylindrically around the sides to simulate the thermal bath that keeps the sample at the required temperature, to prevent pressure waves, and to maintain the shape of the sample [16]. The calculations were performed at 0 K.

3. Results and discussion

Typical craters created by an impact of a normally directed Ar_{872} projectile having kinetic energy of 20 keV, 40 keV and by 40 keV Ar_{872} projectile bombarding the Ag(1 1 1) sample at 70° relative to the surface normal are shown in the Fig. 1. The presented craters are formed during impacts that result in a sputtering yield close to the average value for these particular conditions. It is evident that the size of the craters depends both on the energy of the projectile and on the impact angle. For normal bombardment, the crater formed by 20 keV impact is laterally extended and rather shallow. The increase of the energy of the projectile from 20 to 40 keV results in a formation of a deeper (2.6 nm instead of 1.2 nm) and a slightly wider (6.9 nm instead of 6.1 nm) crater. The shape of the crater formed by an impact of Ar_{872} projectile at normal incidence angle is a consequence of an initial history of the penetrating clusters. Due to its large size Ar_{872} projectile interacts strongly with the sample atoms. The process is almost mesoscopic in that the interaction of a Ar_{872} projectile with the rest of the system is a many body collision in which several projectile atoms simultaneously hit the same target atom [5,17]. The result of such activity, called "cluster effect" [6], is caused by a different mechanism of primary energy deposition as compared to monoatomic projectiles or small clusters like Au_3. The individual atoms in the cluster are not initiating their own collision cascades; rather they are working cooperatively to move the target atoms. One of the consequences of such activity is the generation of pressure waves that propagate in the sample [5,7,16]. Another consequence is related to a significant relocation of atoms, which occurs in front of the cluster during penetration into the sample. This phenomena, called "self amorphization" [6], helps to avoid channeling of projectile atoms, which ensure energy deposition in the near surface region, leading to ejection of many particles. As a result, a large but relatively shallow and azimuthally isotropic crater is formed. Due to a heavier mass of the Ag atoms and a weak interaction between Ag and Ar atoms, almost all Ar atoms are backreflected into the vacuum. Consequently, the implantation of the projectile atoms is minimal. Mechanistic analysis of the Ar_{872} cluster bombardment allows the identification of two phases in the cluster impact. In the first phase, the cluster projectile is deformed upon impact and a high-density, high pressure region is formed at the sample/cluster interface. The stress accumulated in this region is released by propagation of a pressure wave and by a side jetting or splashing of projectile atoms, followed by a slow volume expansion of a flattened cluster [18–21]. The Ar atoms remain confined in the created crater for a few ps. During that time they form a layer that hinders particle emission from the walls and the bottom of the crater. This phenomenon is characteristic to large clusters only, and will not be present for smaller projectiles like C_{60} [22]. In this sputtering phase, most of Ag atoms are ejected from the rim of the formed crater in the fluid like motion. This type of ejection combined with the particle blocking by a cloud of projectile atoms lead to ejection of particles at large polar angles, or so called lateral sputtering [3]. The second phase of sputtering occurs after several picoseconds, when the Ar atoms are spread in a larger volume or are already backreflected into the vacuum. Then, the density of the Ar cloud is reduced to the point where ejection of atoms along the normal direction from the bottom and the walls of the crater is not hindered. However, at this time, most of the primary kinetic energy is already carried away from the impact volume. As a result, only a few particles have sufficient energy to leave the surface, and the ejection efficiency is low along the normal direction. As shown in Fig. 1c, when the projectile is directed at oblique incidence, the modification of the sample almost disappears; i.e. the sputtering yield is close to zero. This is a consequence of efficient energy backreflection from a hard and strongly bound surface at such large impact angles. As barely

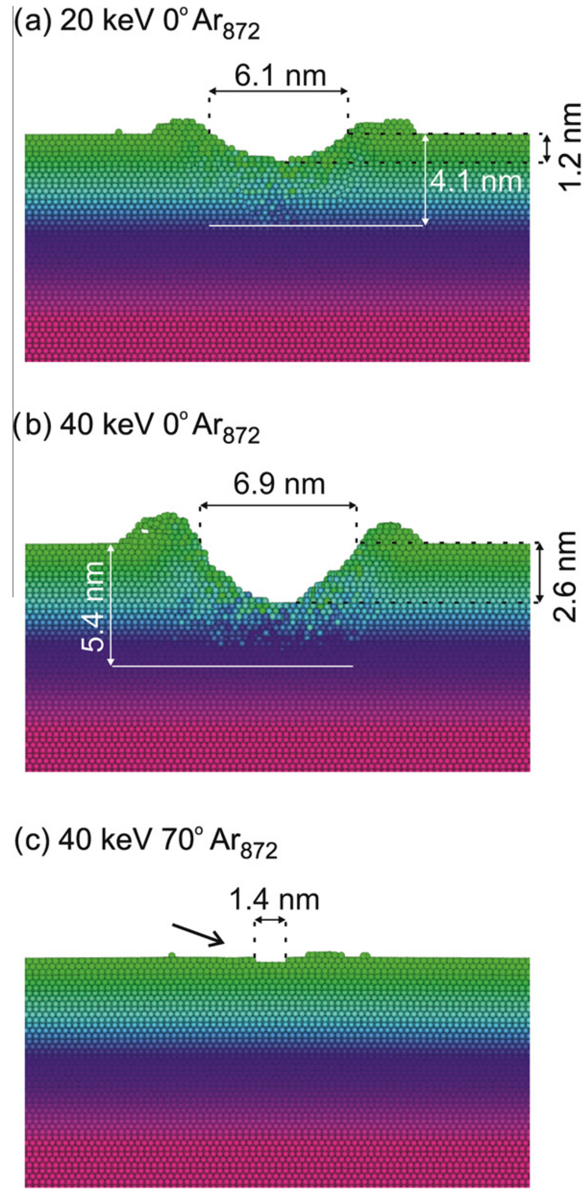

Fig. 1. Cuts through the typical craters formed in Ag(1 1 1) by an impact of (a) 20 keV, (b) 40 keV Ar_{872} at normal incidence, and (c) 40 keV Ar_{872} bombardment at 70° impact angle. The cuts are 1.5 nm wide and are centered at the point of projectile impact. White lines indicated the extent of the crystal volume where atoms are relocated more than a half of the lattice constant from their original position.

20% of the primary kinetic energy is backreflected during 40 keV Ar_{872} bombardment at normal incidence, almost 80% is backreflected at 70° impact angle.

If the general trends observed during individual impacts on a flat surface were preserved during continuous irradiation, one would expect to see a significant difference in the topography of the irradiated surface for different kinetic energy and impact angle of the projectile. The evolution of the sample topography can be quantitatively monitored by the root mean square (rms) roughness of the investigated system. The variation of the rms as a function of the number of impacts or a fluence is shown in Fig. 2. To calculate the rms roughness, the sample was discretized into 0.42×0.42 nm columns, with each column giving a surface height value. This size was chosen in order to be as small as possible for accuracy but large enough so as not to obtain measurements of zero between crystal lattice rows. Two trends can be identified in the development of surface roughness. First, at the beginning, the value of the roughness increases fast. This fast increase is followed by a slow increase that finally goes into saturation. We attribute the initial fast increase to the fact that the roughness of the sample is rapidly changing due to the (artificially) flat surface starting conditions. This phase then moves into the more natural, slow modifications caused by multiple bombardments. As expected from the data shown in Fig. 1, the most corrugated surface is formed after irradiation with 40 keV Ar_{872} clusters at normal incidence. The estimated final roughness value for 40 keV Ar_{872} impacts at normal incidence is 2.2 nm. The roughness decreases with the decrease of the primary kinetic energy. A comparison with our previous study [11] indicates that the roughness decreases also with the increase of the cluster size, if the total kinetic energy is constant. The corresponding value for 20 keV Ar_{872}, C_{60} or Au_3 projectiles is 1.6, 2.4 and 3.1, respectively [11]. The oblique irradiation leads to a less corrugated surface as compared to the normal bombardment. The beam of Ar_{872} projectiles directed at 70° relative to the surface normal, however, also significantly affects the sample morphology, despite the fact that the single impact of such cluster does almost nothing to the irradiated flat surface (see Fig. 1c). As shown in Fig. 2, the estimated roughness is 0.6 nm for 20 keV Ar_{872} and almost 1.1 nm for 40 keV Ar_{872} at 70°. Visual inspection of the resulting surface (not shown here) indicates that the surface erosion has a directional character. Long and narrow valleys are created along the azimuthal direction of projectiles incoming at the oblique impact angle.

It is interesting to verify, if, and to what extent, modification of the surface topography will influence such experimentally important quantities as the sputtering yield or angular spectra. In other words, to what extent the quantities calculated on the flat surfaces will properly estimate the values measured in experiments performed at dynamic conditions. The dependence of the total sputtering yield on the number of impacts is shown in the Fig. 3. Each point in the figure is the running average value of 30 consecutive impacts to reduce statistical uncertainty. It is evident that the sputtering yield depends on the fluence, although the extent of this dependence varies with the impact angle. For normal bombardment and low fluence, the sputtering yield slightly decreases with the fluence. However, this decrease is fast and for fluences larger than 1×10^{13} ions/cm^2 the sputtering yield is almost constant. There is a similarity in the rate of rms change and the rate of decrease of the calculated sputtering yield. In both cases, a fast and slow component can be identified, with the transition point from fast to slow occurring roughly at 1×10^{13} ions/cm^2 for 40 keV projectile. It is justifiable, therefore, to conclude that the yield depends on the surface topography. Similar conclusions have been also made from our previous study with Au_3 and C_{60} projectiles [11]. The calculations performed for a projectile bombarding flat surfaces at normal impact angle will slightly overestimate the experimental values. The comparison of our current data with the calculations performed for 20 keV C_{60} [11] shows that the amount of this overestimation increases with the projectile size.

A quite different variation of the sputtering yield with the fluence occurs when the projectile is directed at the surface at the oblique angle. The number of Ag atoms emitted from the flat surface is low. However, the total sputtering yield strongly increases with the fluence. Such behavior is attributed to the change of the local impact angle. When the substrate is flat the impact angle is large. As a consequence, due to a mass difference between Ar and Ag atoms, most of the projectile kinetic energy is backreflected and cannot contribute to sputtering. These impacts predominantly cause relocation of atoms rather than atoms' emission [7]. However, when the substrate becomes rough, the local impact

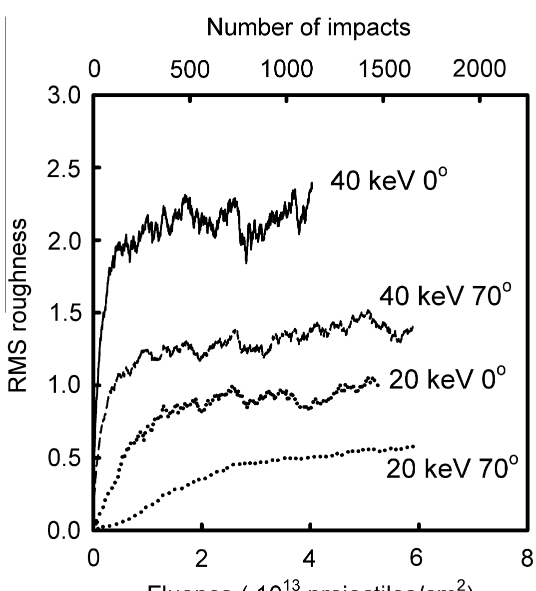

Fig. 2. Dependence of the root mean square (rms) roughness on the number of impacts or fluence for 20 and 40 keV Ar_{872} projectiles bombarding Ag(1 1 1) surface at 0° and 70° impact angles.

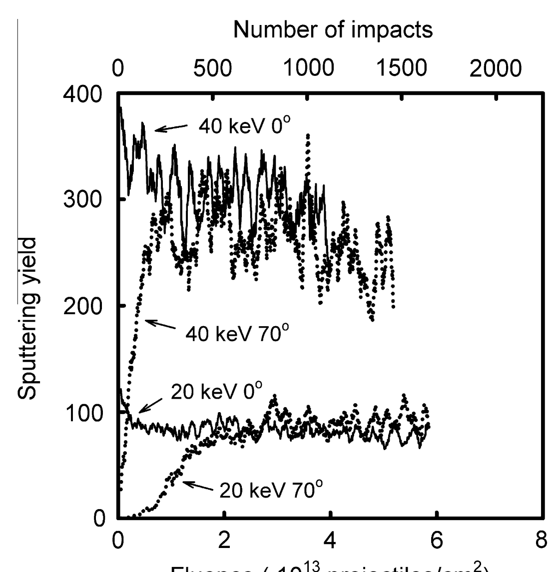

Fig. 3. Dependence of the total sputtering yield on the number of impacts or fluence for 20 and 40 keV Ar_{872} projectiles bombarding Ag(1 1 1) at 0° and 70° impact angles.

angle is reduced. As a consequence, the backreflection process is also reduced and a larger portion of the primary kinetic energy is deposited in the sample leading to a more efficient ejection. Again, there is a similarity in the rate of roughness change and the rate of increase of the calculated sputtering yield. The comparison of the yields calculated for obliquely bombarded flat and rough surfaces shows that the yield calculated on a flat surface is a poor estimate of the yield measured in experiments performed in dynamic conditions.

The observation that the sputtering yield dependence on the fluence is different at different impact angles indicates that the shape of the yield dependence on the impact angle will also change with fluence. Indeed, as it is shown in Fig. 4, the shape of the sputtering yield dependence on the impact angle is different if calculated on flat and roughened surfaces. In the case of a flat surface bombardment, the total sputtering yield decreases with the impact angle. A similar behavior has been observed previously for C_{60} bombardment of a organic material [23] and Ar_n clusters bombarding inorganic samples [23,24]. In general, dependence of the total sputtering yield on the impact angle has been attributed to two counterbalancing effects [25]. The first effect is associated with the energy deposition profile being shifted closer to the surface with the increase of the impact angle. This phenomenon should lead to a yield enhancement if a significant portion of the primary kinetic energy is deposited below the volume that can contribute to ejection at the normal impact. The second effect is associated with the energy backreflection, which becomes particularly important at large impact angles [25]. As the amount of backreflected energy increases, less energy is available for sputtering, and the sputtering yield should decrease [25]. For keV medium and large clusters composed from light atoms almost all of the primary kinetic energy is deposited in the volume that can efficiently contribute to sputtering [23]. As a result, the yield can only slightly benefit (if at all) from the modification of the deposited energy profile. The major role is played by the energy backreflection. As a consequence, the resulting sputtering yield decreases with the impact angle, which is indeed observed for Ar_{872} projectile. Development of the surface topography can influence this scenario in two ways. At large impact angles, the increase of the surface roughness leads to a decrease of the average impact angle. As shown in the data calculated on a flat surface presented in the Fig. 4, this modification should lead to a signal increase. On the other hand, the average impact angle will increase if the impact angle measured at the flat surface is small. This modification should lead, in turn, to a less efficient ejection. As a consequence, the resulting distribution should be flatter and extend to large impact angles, which is indeed observed.

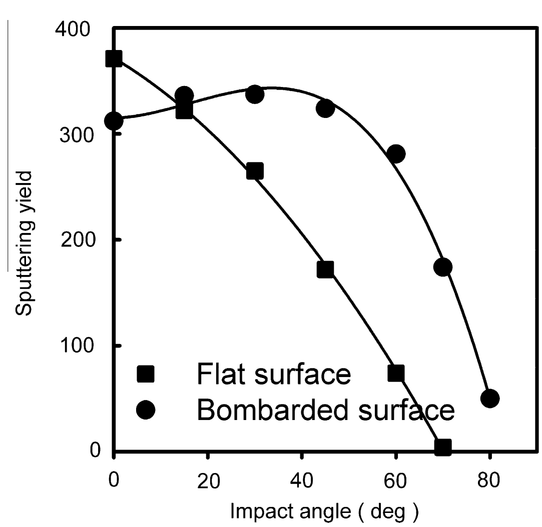

Fig. 4. Dependence of the total sputtering yield of silver atoms on the impact angle for 40 keV Ar_{872} projectile bombarding (a) flat (squares) and (b) preirradiated (circles) Ag(1 1 1) surface. Solid lines are drawn to guide the eye.

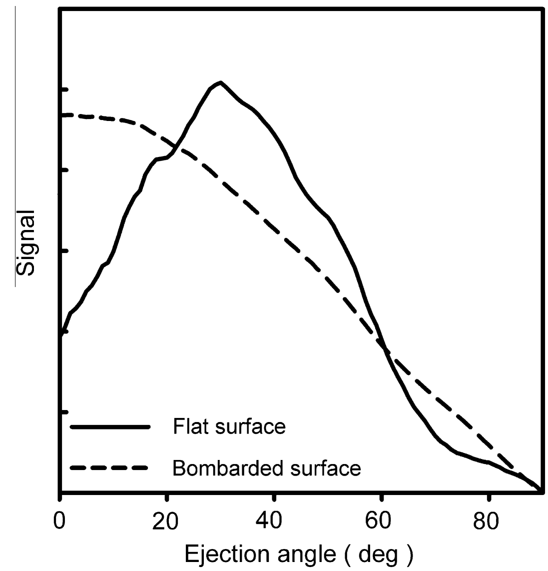

Fig. 5. Angular distributions of the Ag atoms ejected from Ag(1 1 1) bombarded with 40 keV Ar_{872} at 0° relatively to the surface normal. Solid and dashed lines represent spectra collected from a flat and preirradiated (900 impacts) sample, respectively.

The ejection efficiency is not the only experimental quantity that may depend on the surface roughness. Also the ejection angle is sensitive to the local environment. Indeed, as shown in Fig. 5, the most probable emission angle shifts to the surface normal when the surface becomes corrugated. The angular distribution of ejected particles calculated for a flat surface peaks at large polar angle. Such behavior is a consequence of already mentioned emission of substrate particles from the rim of a forming crater and a blocking of silver ejection along the normal direction by a hovering cloud of projectile atoms. The off-normal ejection was not present for keV C_{60} projectiles irradiating silver sample due to a lack of lateral projectile expansion and a cloud blocking [22]. The observed shift of the most probable ejection angle closer to surface normal is caused by a larger diversity of possible impact scenarios. For instance, projectile may impact at the bottom or at the walls of the valleys formed by previous impacts at the modified surface. In both these cases possible ejection angles will be limited by the presence of surrounding crater walls. Moreover, at the corrugated surface there are also numerous protruding structures [10,11]. These structures will also block atoms ejecting at large polar angles. Finally, the local impact angles and inclinations of surface areas from where the ejection occurs will have a wide distribution of possible values, which will also lead to a more uniform angular distribution.

4. Conclusions

The effect of the continuous irradiation by keV Ar_{872} projectiles on the development of surface topography, and the efficiency of material ejection has been examined. It has been shown that the evolution of surface morphology is strongly dependent on both the kinetic energy of the projectile and the impact angle. Two trends in development of the surface morphology are observed. For low fluence, when the surface is almost flat, the rms roughness increases fast, because each impact changes sample corrugation significantly. On the other hand, for large fluence, the global surface roughness becomes constant. There are several predictions that result from our studies. The final roughness of the bombarded surface increases with the kinetic energy of the projectile. If the kinetic energy is constant, less corrugated surfaces can be obtained by increasing the impact angle. Both, the sputtering yield and the angular spectra are sensitive to the ion fluence. The number of ejected silver atoms calculated at a flat surface is slightly larger than corresponding number obtained at corrugated sample. These numbers are, however, significantly different during bombardment at oblique impact angles. The most probable ejection angle is shifted towards the surface normal when the surface is getting corrugated. Also the shape of the sputtering yield dependence on the impact angle is sensitive to the surface morphology. Our study indicates, therefore, that it may not be justifiable to project some results of calculations obtained at flat surfaces to the experiments performed in dynamic conditions.

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