Nanoparticle Ejection from Au Induced by Single Xe Ion Impacts

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In situ transmission electron microscopy has been used to observe sputtered Au during Xe ion irradiation in transmission geometry. The sputtered Au was collected on an electron transparent carbon foil. Nanoparticles were observed on the collector foil after they were ejected by single ion impacts. The ejection is from the melt zone formed during the thermal spike phase of a displacement cascade produced near the surface by a single ion impact. Such single ion impacts are also capable of producing craters. Ejected nanoparticles can make a significant contribution to sputtering.

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Introduction .- Energetic heavy ions impacting on solids impart energy and momentum to atoms in the solid. Through additional collisions, these recoiling atoms distribute their energy in a displacement cascade. Multiple collisions between recoiling atoms can be described by linear transport theory as independent binary collision events as long as the density of recoiling atoms is low. However, when the projectile mass and/or the atomic mass of the substrate are large, these assumptions fail as nonlinear processes occur [1,2]. When the mean free path between collisions is on the order of the atomic spacing, a highly disturbed volume known as an atomic displacement spike or energy spike is created in less than 10^{-13} sec. Within approximately 10^{-11} sec (thermal spike phase) the spike consists of a small volume in which the energy density may be several eV/atom. Such an energy density corresponds to temperatures well above the melting temperature and in some cases may exceed the vaporization temperature of some materials. In addition to the thermal spike, it is to be expected that there will be a corresponding pressure spike. When embedded within a material the recoiling atoms result in zones of damage consisting of atoms displaced from their original lattice positions. When located near a surface, however, the combined effect of temperature and pressure may be to eject material and modify the surface.

Indeed molecular dynamics (MD) simulations indicate that displacement cascades may be distorted by such effects near to a surface. Several effects have been noted in simulations of near-surface cascades, including creation of craters by plastic flow [3,4], the punching of material to the surface by pressure spikes [5], and emission of clusters of small numbers of atoms [6–8]. Also observed for single ion impacts on Au is the rare occurrence of the ejection of large clusters consisting of as many as 800 atoms (3.2 nm diameter) [9]. Similar clusters are calculated to be ejected by impacts on Au [9] and Cu [10].

In addition to MD simulations, near-surface cascades have been modeled analytically, leading to the conclusion that the lack of constraint on near-surface displacement cascades may result in the outward flow of essentially liquid material from the melt zone of the cascade producing a surface crater thus giving broad agreement with the results of the MD work [11]. Attempts to describe particle ejection and sputtering by the pressure spike generated by a cascade in terms of a shock wave have not been successful [12-14].

Experimentally, nonlinear effects in displacement cascades have been recognized in high sputter yields [15], the ejection of small atomic clusters during sputtering of Au [16], and increased yields for molecular ions over single ions [17,18]. In addition, single Xe ion impacts have been observed to give rise to surface craters [19–22]. Produced in association with craters are nanoparticles [21,22] that may appear to be either connected to a crater as a lid or in isolation on the surface. Observation of such nanoparticles raises the possibility that they may have been ejected intact from the surface when a crater formed. This work examines this possibility and shows that nanoparticles are ejected in sufficient numbers to make a significant contribution to the sputtering yield.

Experimental.-In situ ion irradiations were carried out in a Hitachi H-9000 transmission electron microscope (TEM), operating at 300 keV, located at the IVEM/Accelerator Facility located at Argonne National Laboratory [25]. In the IVEM/Accelerator Facility, the ion beam is oriented 30° from the microscope axis. In our experiments, the specimen was tilted 15° towards the ion beam so that both ions and electrons were incident on the specimen at 15° to the foil normal. The ion beam first passed through the specimen before passing through the carbon collector. Specimens were irradiated at room temperature with 400 keV ions at dose rates between 1 and 2×10^{-3} ions $nm^{-2} s^{-1}$. The beam current was continuously measured by an annular Faraday cup system that was calibrated by an internal, removable Faraday cup with an absolute accuracy of 10%. Total doses were small, less than 1 Xe nm^{-2} , so that sputtering, surface roughening and specimen thinning had little effect on the experimental results.

Thin Au films were made by evaporation of 99.999 at. % pure starting material onto NaCl at a temperature of 350 °C. The Au film had a $\langle 110 \rangle$ surface normal, and the thickness was determined by Rutherford backscattering to be 62 ± 1 nm. All specimens were obtained from the same piece of Au-covered NaCl. Small pieces of Au were floated on a water alcohol mixture and picked up on Cu TEM grids. No thin areas or holes were found in the viewed areas of the Au foils before or after irradiation.

Amorphous carbon films, approximately 20 nm thick, on Cu grids [23] were used to collect material sputtered from the exit surface of the specimen. The carbon collector foil and the gold film were separated by between 20 and 40 μ m. With this separation, sputtered Au arriving at the collector could originate from outside of the viewed area. Observations were performed only far from the edge of the TEM grid bars supporting the Au and from the edges of the Au specimen. TRIM [24] calculations for sputtered Au atoms and their subsequent impact on carbon indicate that, given their energies, all were stopped on or in the near surface region of the carbon foil. At the low ion doses and Au coverages achieved on the collector foils, resputtering of collected Au is not a concern.

The electron beam passed through both the Au thin film and the carbon collector foil. By adjusting the specimen height in the TEM, it was possible to view either the carbon foil or the gold film with the other contributing an out-of-focus background to the image. Although the Au thin film somewhat obscured the image, gold accumulated on the collector foils could be observed as a bright-field image. Particles of approximately 1 nm in diameter were the smallest that could be resolved against the combination of out-of-focus background and speckle from the amorphous carbon. TEM images were viewed during irradiation by means of a Gatan 622 video camera and image-intensification system. The total area of view in the video is 110 nm \times 85 nm. The video images were viewed with total magnifications of approximately 2×10^{6} , and recorded on videotape with a time resolution of 1/30th sec (a single video frame). Images recorded on video have a total field of view into which approximately 20 ions arrived every second (30 video frames). Experimental details, including the total ion dose, were recorded on each video frame. Post-irradiation, high-resolution TEM observations of the Au nanoparticles on the carbon collector were made with a JEOL-4000 EX operating at 400 keV and a JEOL 3010 operating at 300 keV.

Results and discussion.—Material sputtered from the back surface of a 62 nm thick Au film during a 400 keV Xe irradiation at room temperature was collected on a carbon film. The sputtered material is distinguished by the appearance of nanoparticles. Arrival of nanoparticles on the collector is illustrated in Fig. 1. This figure is a composite of images extracted from single frames of a video recording over a time during which 116 ions impacted the specimen in an area the size shown in the figure. Dark



FIG. 1. Nanoparticle collection during 400 keV Xe irradiation of Au. Frames (a) and (b), and (c), and (d) are separated in time by a video frame.

spots in the figure are Au nanoparticles. High-resolution images show each nanoparticle to be multiply twinned as would be expected for material ejected in the liquid state from the melt zone of a displacement cascade. Displayed in Fig. 1 is the particle-by-particle arrival within one area that is a small fraction of the viewed area. This sequence is typical of all sputtering events observed during six independent repetitions of the Xe irradiation. Note that the appearance of a new nanoparticle does not disturb existing nanoparticles. Even the arrival of the large nanoparticle in the last frame leaves unchanged the two smaller nanoparticles to its left and above. No nanoparticles appeared when the ion beam was turned off.

Nanoparticle arrivals at the collector foil are well separated in time and space because ions impact the viewed area at a rate that is less than one per video frame and the particle production rate is about 1%. Frame-by-frame examination of the recordings made during irradiations reveals that particles appear on the carbon collector within the 1/30 sec required for the recording of a single video frame. The total area of view in the video is 9.35×10^3 nm². During the time required to record an image the mean number of ions arriving in this area is approximately 0.14—significantly less than one—leading to the conclusion that nanoparticle ejection is caused by single ion impacts.

This low nanoparticle ejection rate allows accurate determination of the ion dose at which each particle arrives. The video frame on which every nanoparticle first appeared during 400 keV Xe irradiation was determined along with the total ion dose at the time of arrival. Accumulation of nanoparticles during a 400 keV Xe irradiation is graphically displayed in Fig. 2. Nanoparticle deposition commences from the start of the irradiation, and over the dose range shown, the accumulation appears to be linear. The slope of Fig. 2 yields a nanoparticle collection rate of 0.011 particles/Xe. The detection limit for nanoparticles is 1 nm so this rate does not include either small clusters or individual Au atoms.

Ejected nanoparticles vary in size from the detection limit of 1 nm to about 9 nm. The most common size of visible nanoparticles produced by 400 keV Xe irradiation is 3 nm. With this as a mean size and assuming that the nanoparticles on the collector foil are hemispherical in shape, a collection rate of 0.011 particles/Xe implies that nanoparticles would contribute 4.6 Au/Xe or 11% to the transmission-sputtering yield of 40 [26]. This represents a very important contribution to sputtering from nonlinear collisional processes in displacement cascades.

With a few exceptions for the largest particles, the nanoparticles on the carbon collector foil do not migrate or exhibit other signs of ion impacts during continued ion irradiation. Resputtering by the keV Xe ions that had passed through the Au film was also very low in contrast to that caused by ionization during MeV ion irradiation of Au islands evaporated on carbon foils [27]. When the nanoparticles are large, it is possible for a Xe ion impact to produce a recoil event in the particle that causes it to jump a fraction of its diameter. Such an event is illustrated in Fig. 3. Shown in Fig. 3 are successive video frames displaying movement of a 5 nm diam particle during the time required to record a video frame. Although the image of the nanoparticle indicates that its diameter decreased slightly, its volume cannot be accurately estimated because any change of its thickness is unknown. During the time required to record the jump, fewer than 3×10^{-3} ions impacted an area $4\times$ the area of the nanoparticle leading to the conclusion that its motion was caused by a



FIG. 2. Accumulation of nanoparticles during 400 keV Xe irradiation of Au.

single ion impact. No nanoparticle motion was detected after the ion irradiation was stopped. During *ex situ*, high-resolution TEM observations with 300 and 400 keV electrons, Au nanoparticles on the collector foils did not move, although their internal structure changed as has been reported previously [28]. During the ion irradiations, the microscope resolution was insufficient to resolve if such structural changes occurred. The motion events recorded during ion irradiation are due to ion impacts and not the electron beam used to observe the nanoparticles. Simple calculations show that nanoparticle motion cannot be the result of simple momentum transfer between a Xe ion and the Au nanoparticle.

As would be expected, such motion events are rare and difficult to detect even for such large particles and only 5 were noted during the many irradiations. Although the experiments reported here stopped at low doses, other experiments have revealed that continued nanoparticle deposition to higher density on the collector foil eventually results in particle coalescence and incorporation of newly deposited nanoparticles into existing material. This results in the growth of a continuous Au thin film on the collector. As the Au coverage and thickness increases, the effects of ion impacts begin to be seen on the deposited material. This is associated with the ability of a particle or film to retain the energy deposited in atomic recoils in a displacement cascade caused by a single ion impact. In addition, single Xe ion impacts on nanometer size protuberances of Au cause reshaping that resembles local melting [20]. Motion occurred only in particles 5 nm or more in diameter. Particles this size might be capable of retaining the energy of an ion impact. The implications are that the nanoparticle motion was associated with melting caused by a displacement cascade retained by the particle. Unfortunately, such detail could not be observed.

When an irradiation is capable of producing dense displacement cascades in the near-surface region of a specimen, craters are formed [21,22]. Single 400 keV ion impacts produce craters on Au as large as 12 nm in diam on the irradiated surface but with more small than large craters. *In situ* TEM observations found particles attached



FIG. 3. Change in position of a nanoparticle caused by a single Xe ion impact. Frames (a) and (b) are separated in time by a video frame.

to a few crater rims as well as lying on the surface not associated with a crater. Occasionally more than one particle was attached to a crater; however, most craters did not have attached particles. The production rate of all sizes of craters on the exit surface of the Au foil of a 62 nm thick au foil is approximately 0.03 craters/Xe. This rate indicates that the nanoparticle ejection rate is a large fraction of the crater production rate and may explain why only a few craters have associated nanoparticles.

We associate the ejection of nanoparticles and crater formation with the thermal spike phase of displacement cascades produced by single ion impacts. Highresolution TEM shows the nanoparticles to be multiply twinned and faceted as would be expected for material ejected in the liquid state from the melt zone of a displacement cascade. In addition, craters on Au are faceted. Both nanoparticle ejection and crater formation are massive events on the atomic scale. The common features of the two effects, including similar sizes and rates, strongly suggest a common origin in the near surface, displacement spikes produced by single ion impacts. This is strongly supported by computer simulations of displacement events at a surface [3,4,8,23].

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- [1] J.A. Brinkman, J. Appl. Phys. 25, 951 (1954).
- [2] J.A. Brinkman, Am. J. Phys. 24, 246 (1956).
- [3] M. Ghaly and R.S. Averback, Phys. Rev. Lett. 72, 364 (1994).
- [4] M. Ghaly, K. Nordlund, and R. S. Averback, Philos. Mag. A 79, 795 (1999).
- [5] K. Nordlund, J. Keinonen, M. Ghaly, and R. S. Averback, Nature (London) 398, 49 (1999).

- [6] G. Betz and K. Wien, Int. J. Mass Spectrom. Ion Process 140, 1 (1994).
- [7] G. Betz and W. Husinsky, Nucl. Instrum. Methods Phys. Res., Sect. B **102**, 281 (1995).
- [8] T.J. Colla and H.M. Urbassek, Comput. Mater. Sci. 6, 7 (1996).
- [9] T.J. Colla and H.M. Urbassek, Nucl. Instrum. Methods Phys. Res., Sect. B 164–165, 687 (2000).
- [10] T. J. Colla, H. M. Urbassek, A. Wucher, C. Staudt, R. Heinrich, B. J. Garrison, C. Dandachi, and G. Betz, Instrum. Methods Phys. Res., Sect. B 143, 284 (1998).
- [11] R.S. Averback and M. Ghaly, J. Appl. Phys. 76, 3908 (1994).
- [12] M. Guinan, J. Nucl. Mater. 53, 171 (1974).
- [13] G. Carter, Radiat. Eff. Lett. 43, 193 (1979).
- [14] Y. Kitazoe and Y. Yamamura, Radiat. Eff. Lett. 50, 39 (1980).
- [15] D. A. Thompson and S. S. Johar, Appl. Phys. Lett. 34, 342 (1979).
- [16] H. L. Bay, H. H. Andersen, W. O. Hofer, and O. Nielsen, Nucl. Instrum. Methods 132, 301 (1976).
- [17] H.H. Andersen and H.L. Bay, J. Appl. Phys. 45, 953 (1974).
- [18] H. H. Andersen, A. Brunelle, S. Della-Negra, J. Depauw, D. Jacquet, and Y. Le Beyec, Phys. Rev. Lett. 80, 5433 (1998).
- [19] K. L. Merkle and W. Jäger, Philos. Mag. A 44, 741 (1981).
- [20] R. C. Birtcher and S. E. Donnelly, Phys. Rev. Lett. 77, 4374 (1996).
- [21] S. E. Donnelly and R. C. Birtcher, Phys. Rev. B 56, 13599 (1997).
- [22] S.E. Donnelly and R.C. Birtcher, Philos. Mag. A 79, 133–145 (1999).
- [23] C foils from Fullam Inc., catalog No. 11250.
- [24] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Ranges of Ions in Solids* (Pergamon Press, New York, 1985).
- [25] C. W. Allen, L. L. Funk, and E. A. Ryan, Mater. Res. Soc. Symp. Proc. 396, 641 (1996).
- [26] R.C. Birtcher and S.E. Donnelly, Mater. Res. Soc. Symp. Proc. (to be published).
- [27] H. H. Andersen, H. Knudsen, and P. Moller Petersen, J. Appl. Phys. 49, 5638 (1978).
- [28] S. Iijima and T. Ichihashi, Phys. Rev. Lett. 56, 616 (1986).
- [29] M. H. Shapiro and T. A. Tombrello, Surf. Sci. 453, 143 (2000).