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Electron Microscope Examination of the Surface Topography of Ion-Bombarded Copper

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Transmission electron microscopy of thin, polycrystalline copper foils has revealed the formation of a sputtering structure after bombardment at normal incidence with Xe^+, Cu^+, or Pb^+ ions of 50 to 80 keV energy. In general, the surface of each individual grain degenerates into a "hill and valley" structure, so as to develop those {100} faces lying nearest to the plane of the surface. The sputtering structure has been found to be independent of any prior electropolishing surface structure. Similarity between the spacing and crystallographic direction of the sputtering structure, and the general appearance of the dislocation arrays produced by ion bombardment, suggests that these dislocations could influence the initiation of the structure. A tentative model based on this hypothesis is proposed to account for the periodicity of the observed sputtering effect.

1. Introduction

It is well known that ion bombardment of solids results in the formation of a surface structure which is a consequence of preferential sputtering. Examples of this phenomenon were reported at a CNRS* symposium [1], and have also been discussed and reviewed (e.g. references 2 and 3). Previous experimenters have reported a variety of different surface effects depending on whether or not their targets were polycrystalline or monocrystalline and on the energy and angle of incidence of the ion beam to the target. Optical microscopy has commonly been used to study sputtering structure, with the result that only gross detail is observed; however, the use of replica electron microscopy (e.g. references 1, 4, and 5) and scanning electron microscopy [6] have extended the limit of resolution to below 1000 Å.

In the present paper, we describe a technique using transmission electron microscopy to record the detailed structure produced on thin, polycrystalline metal foils bombarded at normal incidence with Xe^+, Cu^+, or Pb^+ ions of energies between 50 to 80 keV. In this case, the limit of resolution is better than 50 Å and, together with selected-area electron diffraction, permits the detailed examination of the individual single-crystal grains, both for their surface structure and for the fine-scale dislocation arrays produced in their lattice by the bombardment.

2. The Experiment

2.1. Specimens

Thin, polycrystalline copper foils (Johnson Matthey†, spectrographically standardised, 25 μm thick, rolled foil) were annealed for 2 h at 750° C in vacuum so as to produce a grain size of about 15 μm. Thin sections ($\sim$2000 Å) suitable for transmission electron microscopy were prepared by electropolishing the foils in H_3PO_4/H_2O solution. These were fixed between folding, 100/200 mesh, copper, electron microscope specimen grids and were mounted in the target chamber of a 150 keV heavy ion accelerator, which was subsequently evacuated to $\sim 10^{-6}$ torr. Some ion bombardments were also carried out on punched-out, 2.3 mm diameter discs of copper, having the same specification

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as the foils, and these were prepared for electron microscopy by a jet-polishing technique.

2.2. Irradiations

The thinned specimens were bombarded at normal incidence with magnetically analysed beams of Xe^+, Cu^+, or Pb^+ ions in the energy range 50 to 80 keV, at a dose rate which was sufficiently low that the specimens' temperature increase during bombardment was no more than a few degrees above room temperature. In most irradiations, the foils were partially shielded from the ion beam by their electron microscope specimen support-grids, and this effectively produced adjacent, bombarded and unbombarded regions, which were useful for comparison between control material and irradiated material. After bombardment, the foils were examined by transmission electron microscopy and analysed by selected-area electron diffraction.

2.3. Electron Microscope Observations

In almost every specimen examined, whether thin, supported film or disc, a regular surface structure appeared after bombardment with Xe^+, or Pb^+, or Cu^+, to an ion dose which was sufficient to cause the removal of at least 300 Å of copper, as estimated from available sputtering-ratio data [7]. The structure was different for differently oriented grains within the specimen, and its formation was not affected by the presence or absence of the screening grids. In the particular case of grains oriented with their (110) or (310) planes parallel to the surface, aligned bands of light and dark contrast were readily apparent; but, in the case of (111)- and (112)-oriented grains, the dark contrast exhibited a "cellular" type of appearance. On the other hand, grains oriented with their (100) planes parallel to the surface, exhibited no detectable contrast structure, even after extended bombardment. Figs. 1, 2, 3, and 4 illustrate the general nature of these results for several different orientations. Fig. 1 shows that, whenever the overlaid grid bar has been removed after bombardment, its profile is delineated at the boundary between the sputtered and thicker, shielded areas, and that the periodic contrast has only occurred in the bombarded areas. In all grains, extensive radiation damage in the form of an entangled network of dislocations is observed, but it should be noted that this appears at doses very much lower than that necessary for the development of any band structure.

The variation of contrast is a consequence of greater electron absorption and scattering in this banded structure, and arises from local changes in film thickness, suggesting the presence of an undulating surface structure. Since this structure is not present in the unbombarded areas of the copper, it must have resulted from a non-uniform sputtering, which preferentially develops certain crystal faces. In the vicinity of thin edges, this effect often produced local perforation of the foil.

In fig. 1, three differently oriented grains are visible, and it is readily apparent that the surface structure bears some relation to the relative orientation of the grains with respect to the ion beam. Selected-area electron diffraction patterns taken from (110) and (310) grains show that the regular "hill and valley" structure is aligned in the $<001>$ directions parallel to the foil surface. This is illustrated in fig. 2, where three grains having (110), (310), and (100) orientations are visible in the same field of view. The dark contrast bands lie in the [001] directions of the (110) and (310) grains, whilst the (100) grain has no detectable preferential-sputtering structure. Irradiation-produced dislocation entanglements appear in all three grains. A cross-sectional profile of the sputtering structure is shown in fig. 3, where the cellular pattern of a (211) grain is delineated at an inclined grain boundary lying between a (310) and a (211) grain. The profile of the sputtering structure at the edge of the (211) grain is clearly seen to be periodic, with a repeat distance of about 2800 Å. Closer examination and geometrical analysis of many different grains leads to the conclusion that it is the {100} *surfaces* which develop preferentially by selective sputtering as the grain surface is eroded away.

To investigate the evolution of the sputtering structure, a copper film was given successive bombardments with 60 keV Xe^+ ions and was examined in the electron microscope after each bombardment. Initially, after a dose of $\sim 4 \times 10^{16}$ ions/cm^2, only heavy dislocation damage was observed, and in some grains these tended to become aligned in the $<001>$ directions lying in the plane of the specimen (as an example, see fig. 5).

The "furrowed" structure was first detected at a dose of $\sim 6 \times 10^{16}$ ions/cm^2 and, at this threshold dose, exhibited the same periodicity

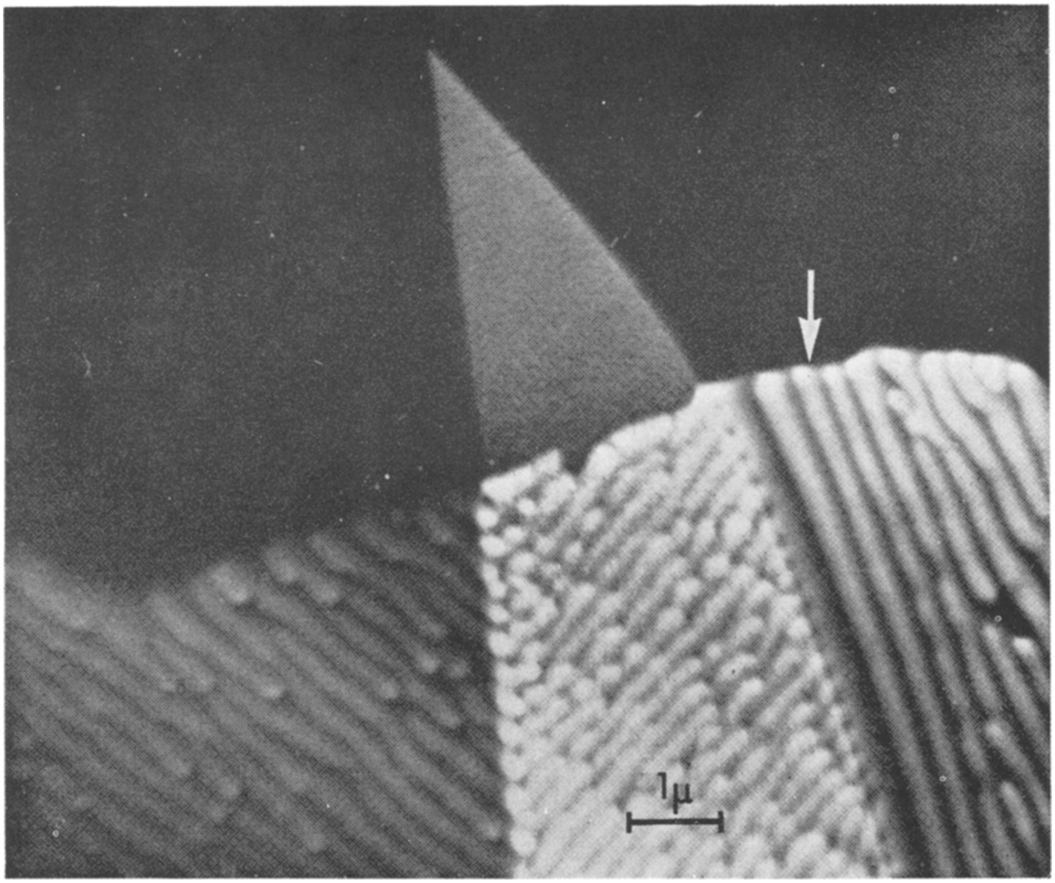

Figure 1 Transmission electron micrograph of a copper film after bombardment with $\sim 2 \times 10^{17}$ 60 keV Xe^+ ions/cm^2. A bar of the support grid has been displaced after bombardment, and its outline (arrowed) forms the boundary of the ion-bombarded area, which contains broad, aligned bands of light and dark contrast.

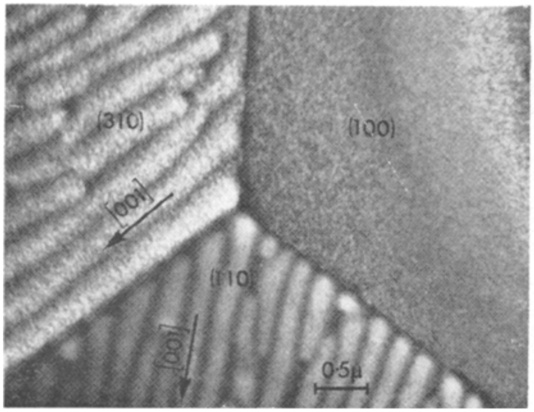

Figure 2 Micrograph showing the junction of three differently oriented grains. The sputtering bands which appear in the (110) and (310) grains are aligned in [001] directions; no band shave formed in the (100) grain. Ion dose as for fig. 1.

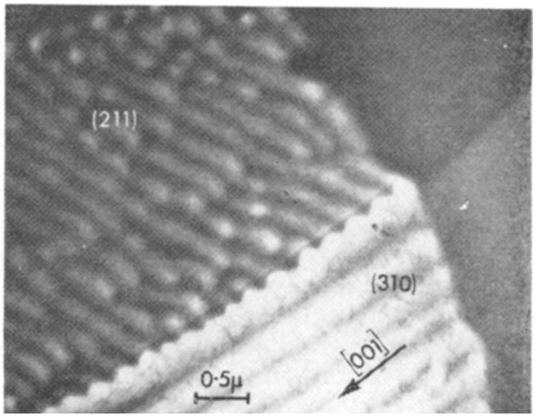

Figure 3 Inset from fig. 1 showing sputtered (211) and (310) grains. The (211) grain has a "cellular" sputtering structure, and its profile is delineated at the inclined grain boundary.

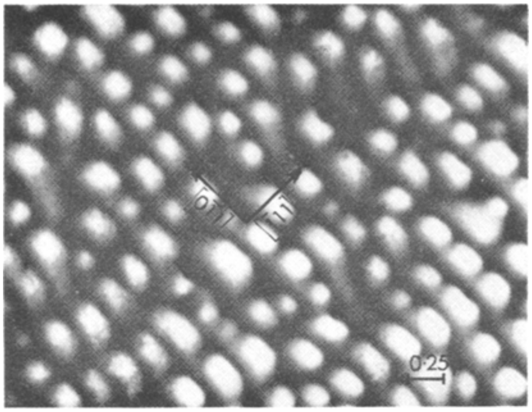

Figure 4 Detail of "cellular" (211) sputtering structure. Ion dose as for fig. 1.

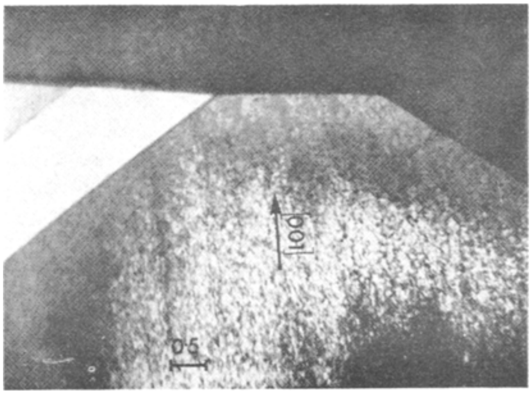

Figure 5 Micrograph demonstrating the tendency for alignment of irradiation-induced dislocations. Ion dose ~4 × 10^{16} 60 keV Xe^+ ions/cm^2.

as that of the well-developed structure seen after prolonged sputtering. This is shown in fig. 6, where the "furrows" have developed in the vicinity of several stacking faults within the grain. It is apparent that the "furrows" are delineated on one edge of the fault only. It can be inferred that the faults are intersecting both top and bottom surfaces of the specimen; therefore, one edge of a fault defines the sputtered structure of the bombarded surface, and the opposite edge defines the magnitude of any surface structure that is present after the preparative electropolishing of the foil. In this instance, the sputtering has developed an asymmetrical structure exposing those {100} planes closest to the surface of the foil. Also, it is apparent that, if any electropolishing structure is present, it is not readily detectable in this micrograph. However, in some cases, an electropolishing structure can be formed with a similar appearance and periodicity to that of the sputtering structure, but, as fig. 7 shows, these structures do not lie in the same crystallographic direction.

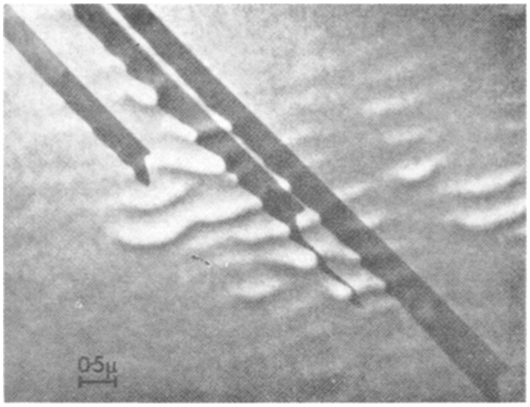

Figure 6 Electron micrograph showing the sputtering structure at an early stage of development. A projection of the "furrow" profile can be seen on one edge of the inclined stacking faults. Ion dose ~6 × 10^{16} 60 keV Xe^+ ions/cm^2.

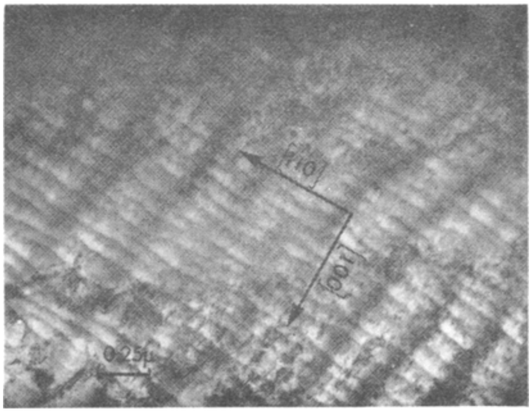

Figure 7 Transmission electron micrograph of a (11 0)-oriented copper film after bombardment at 25° C with 80 keV Cu^+ ions. The electropolishing structure lies in the [11 0] direction, but the sputtering structure (broad, dark bands) is developing in the [001] direction.

Bombardment at ~400° C with Xe^+, Cu^+, or Pb^+ ions did not produce the sputtering structure, even though the ion doses used would have been more sufficient to produce a structure at room temperature.

Lower dose bombardments of Cu^+ ions into copper at ~400° C did, however, produce aligned dislocation arrays. Fig. 8 shows these edge dislocations, which become aligned in the [001] direction in the plane of a (110) surface during bombardment at 400° C with 80 keV Cu^+ ions to a dose of 6×10^{16} ions/cm^2. At this temperature, the dislocations are able to rearrange into their lowest energy configuration and it is interesting to note that the direction and spacing of this array tends to be similar to that of the sputtering structure developed at room temperature.

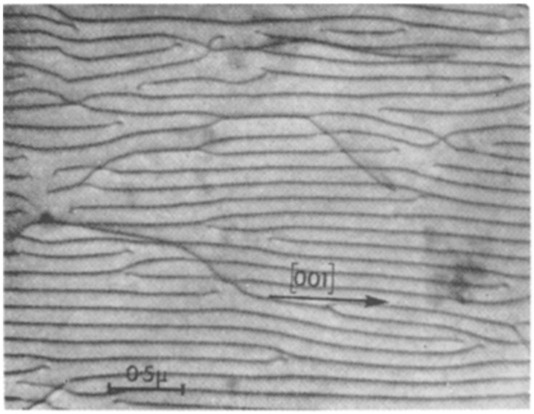

Figure 8 Dislocations aligned in the [001] direction in the plane of a (110) film after an anneal for 1 h at 500° C, following bombardment at 400° C with $\sim 6 \times 10^{16}$ 80 keV Cu^+ ions/cm^2.

3. Discussion

It is well known that different crystal faces have different sputtering rates when bombarded at normal incidence. This is a consequence of three main phenomena.

(*a*) If the ions are incident along a low index direction, then ion-channelling will determine the energy density deposited in the surface layers and hence the fraction of energy available for sputtering [8, 9].

(*b*) Atomic ejection occurs preferentially in the close-packed crystal directions, which in the fcc structure are the $<110>$; the total sputtering yield will therefore depend on the number of these directions which intersect the surface [10].

(*c*) The sputtering yield is strongly dependent on the binding energy of an atom to the surface; different crystal faces have different values of binding energy, which will therefore influence the sputtering from differently oriented grains [7].

It is thus clear that each grain of a polycrystalline specimen will sputter at a different rate (depending upon orientation), with the result that an irregular structure varying in depth from grain to grain will develop on the surface. However, in this paper, we are concerned with the detailed structure that is formed on each individual grain, where differential sputtering cannot be explained so simply.

Thompson [15] has explained the structure which appears around impurity or oxide particles in the surface layers of polycrystalline tin during ion bombardment at normal incidence (see reference 6) in terms of the variation of sputtering ratio with angle of incidence. He shows that, as the surface is steadily removed from around the more slowly sputtered oxide or impurity particle, a structure which takes the form of cones or spikes will develop so as to expose those faces having the highest sputtering rate. For a polycrystalline or an amorphous surface, this happens if the ion beam makes an angle of between 10 and 20° to the crystal surface. However, in the case of a monocrystalline surface, provided the incident ions are always along the same crystal direction so that channelling effects can be ignored, the sputtering rate will depend to a first approximation on the number of close-packed $<110>$ directions which intersect the surface, and on the surface binding energy. On the other hand, not all close-packed directions result in equal atomic ejection, and this will depend both on the angle that each direction makes with the surface and on their relative angle to the ion beam. In this paper, we will not discuss in detail which crystal faces are likely to have the highest sputtering ratio for different angles to the ion beam. However, our observations suggest that, in the case of copper bombarded with 60 keV Xe^+, Pb^+, or 80 keV Cu^+ ions, the {100} faces develop preferentially and are therefore associated with the highest sputtering rate. A consideration, based on current theories of sputtering, of the relative amounts of material sputtered from the various low-order crystal faces of a fcc crystal shows that preferential development of {100} is quite reasonable.

It is not immediately obvious why a sputtering structure of this scale should initiate on a perfectly smooth, single-crystal surface, although, if it is possible to imagine that an initial defect such as a small etch pit exists in the surface, then the development of high-sputtering-rate planes could proceed. For instance, a regular, chemical etching structure, if correctly oriented, could provide an ideal foundation for selective sputtering, but, as fig. 7 shows, this mechanism does not apply in this particular instance.

However, sputtering structures are known to develop from flat, unetched surfaces, and the observation illustrated in fig. 6 suggests that the periodicity of the sputtering structure does not significantly alter as it develops during subsequent ion bombardment. We must therefore look for some regular defect structure produced as a consequence of ion bombardment, and which is responsible for initiating the sputtering structure in a regular periodic way. As suggested by Castaing and Jouffrey [12], dislocations could be important in this respect.

It is well known that, after extended ion bombardment, a complex dislocation network grows from the agglomeration of point defects which are produced by atomic displacement within the sample. Such dislocations are always observed in the bombarded foils and can be seen in the background of the electron micrographs in section 2.3. These dislocations are often observed to interact and line-up in a crystallographic manner (figs. 5 and 8), with a periodicity somewhat similar to the sputtering structure which eventually develops.

We now present a tentative hypothesis to account for the periodicity of the structure, invoking a model based on dislocation line-up. The average depth of penetration of 60 keV Xe^+ ions in copper is about 100 Å, whereas a typical foil thickness is of the order of 2000 Å. The dislocation entanglement produced by the bombarding ions will therefore extend to a similar depth (i.e. 100 Å), and, as such, introduces an asymmetrical stress across the foil. It is difficult to estimate the magnitude of this stress, but a comparable experiment in graphite has shown that it is quite sufficient to cause a monocrystalline surface to degenerate completely, by dislocation reactions, into a twinned structure during ion bombardment [11]. In copper, no significant twin formation is observed, but the stress can influence the configuration of the dislocations, which can move by slip and climb into an equilibrium array so as partially to relieve the stress. These processes (especially climb) are limited by the supply of vacancies, which, at room temperature, can only come from the irradiation-induced point defects. During bombardment at elevated temperatures, thermal processes can assist the attainment of spatial equilibrium, as can be inferred from the array of dislocations in fig. 8. Different crystal orientations will produce different dislocation arrays, since the extra atomic planes which are bounded by the dislocation lines can only lie in certain specific orientations.

The question then arises: how can the dislocation arrays influence the sputtering structure; and can the implanted ions themselves affect the formation of the structure? It is possible that the implantation of inert-gas ions or Pb^+ ions could lead to the formation of either small gas bubbles or lead precipitates, which could nucleate on the aligned bands of dislocations. If these lay just below the surface, they would be exposed as sputtering proceeds, thus producing rows of surface artifacts. The exposed bubble surfaces would then be similar to etch pits and, therefore, could possibly act as initiation sites for the sputtering structure. The lead precipitates would be expected to have a higher sputtering rate than the copper matrix [13], again leading to the initiation of a sputtering structure. However, a similar sputtering structure forms when copper foils are bombarded with 60 keV Cu^+ ions to a dose of 4×10^{17} ions/cm^2. Clearly, in this self-ion bombardment, neither of the above precipitation mechanisms is applicable. We conclude, therefore, that the aligned dislocation bands themselves may well initiate the sputtering structure.

In the vicinity of a dislocation line, the local strains in the lattice fall off inversely as the distance from the dislocation line, so that, even at 10 atomic distances from the dislocation core, the strains are still significant. If the dislocation is very close to a surface, these strains can modify the local conditions so as to reduce the binding energy of an atom to the surface, the sputtering yield will be correspondingly *increased*. Thus, as the surface is steadily removed by sputtering, small furrows might easily form in the vicinity of the dislocation lines as the sputtered surface approaches. These furrows could then act as the nucleation centres for the "hill and valley" structure which subsequently develops. Clearly, for this process to occur, it is not necessary for every dislocation line to be aligned in a regular array: an overall tendency towards alignment would suffice.

In the case of a (100) grain of copper, although dislocation lines meet the surface as it steadily recedes, a sputtering structure does not develop because it is this (100) surface which has the highest sputtering yield, and it will therefore persist and not be perturbed by the underlying dislocation array.

The observations have further shown that, whereas dislocation alignment can occur during bombardment at ~400° C (see fig. 8), the sputtering structure does not form at this temperature. This apparent anomaly may be explained in terms of surface diffusion which is reported to be high for copper at this temperature ($D_S \sim 10^{-7}$ cm^2/sec [14]). Minor surface irregularities caused by the bombardment would therefore rapidly smooth over, with the result that no sputtering structure would develop.

4. Conclusions

(*a*) Heavy doses of 60 keV Xe^+, Pb^+, or Cu^+ ions at normal incidence on copper foils produce a regular "hill and valley" surface structure attributable to surface sputtering. The ion dose required to produce this effect is proportional to the sputtering ratio of the ion used. At the threshold of detection, and when fully developed, the undulating structure has a periodicity of the order of 0.3 μm.

(*b*) The structure exhibits a marked crystallographic relationship to the orientations of the specimen grains. In general, there is a tendency for {100} surfaces to develop. Thus grains oriented such that {100} planes are normal to the incident ion beam do not degenerate into the undulating structure observed for other orientations.

(*c*) There is evidence to suggest that regular chemical etching or electropolishing structures are not responsible for the initiation of the sputtering structure.

(*d*) Similarity between the sputtering structure and dislocation arrays produced by ion bombardment suggests that dislocation lines might play a role in providing the defects from which the structure develops. This hypothesis involves the preferential sputtering of material in the vicinity of a dislocation.

(*e*) Sputtering structure has been found to occur during bombardment with Cu^+ ions. It is inferred from this observation that inert-gas bubbles or precipitates, which could form during bombardment with either Xe^+ or Pb^+ ions, have little or no effect on the initiation of the "hill and valley" structure.

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