DISCUSSION

Brandon, D. G.: I should like to question of the evidence for the penetration of xenon in gold obtained by Gillam. I don't think that his specimen preparation and xenon detection techniques are sufficiently sensitive to detect penetration with the accuracy claimed.

Beeler, J. R.: Gillam's results for xenon penetration are at least a factor of 13 and at most a factor of over 30 times larger than that predicted by Nielson theory, the latter figure pertaining to low energy bombardment (400 eV) and the former to higher energy bombardment (4000 eV). Even if his results were too large by a factor of 2–3 they still indicate anomalously large penetration. They suggest tunnel trajectories because focusing schemes do not apply to primary radiation particles.

Vineyard, G. H.: How did you determine which of the close pairs were stable?

Beeler, J. R.: The results of Gibson, Goland, Milgram and Vineyard for unstable configurations in copper were used as a basis for determining unstable defect configurations.

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Collision Processes in Ion Irradiation and Sputtering Deposit Patterns in Zinc and Germanium

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Sputtering deposit patterns from various planes of single crystals of zinc and germanium were observed. These patterns cannot be explained by the focusing collision chains in usual sense. Tentative explanations for these patterns were proposed.

1. Introduction

Sputtering deposit patterns of noble metals such as gold, silver and copper bombarded by argon, krypton, or xenon ions of energies ranging from 1 to 10 keV are interpreted as due to the ejection of atoms from metal crystal in ⟨110⟩ directions. Nelson and Thompson[1] consider that this kind of deposit patterns is an evidence for the focused collision of atoms in f.c.c metals. It will be interesting, therefore, to investigate sputtering deposit patterns of other crystals than f.c.c. metals.

Results for zinc and germanium will be presented in this paper. As zinc has a close-packed hexagonal lattice, one might consider that focused collisions would occur along the closed-packed row of atoms. As germanium has a diamond lattice, in which atoms are not close-packed, one would not expect focused collisions to occur. These are the points to be discussed in this paper.

2. Experimental Procedures

The method of forming a beam of ions is similar to that of Keywell[2] who used a Philips ionization gauge discharge as a source of ions. Ions can be accelerated to an energy range from 1 to 10 keV in our apparatus. Sputtered atoms from the target (specimen) are received by a thin glass plate (collector) to form a sputtering deposit patterns as shown in Fig. 1. This experimental arrangement gives deposit patterns which are

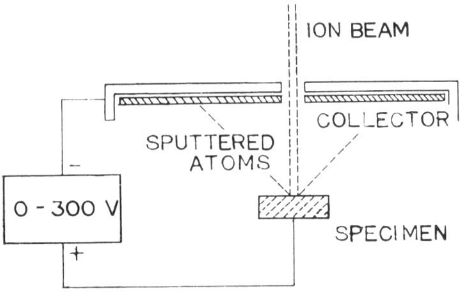

Fig. 1. Experimental arrangement showing specimen and collector.

quite similar to those obtained by Nelson and Thompson[1], if we use noble metals, *e.g.* silver, as a target.

3. Experimental Results

Typical deposit patterns of zinc and germanium are shown in Figs. 2, 3 and 4. The ion beams used were 8 keV argon, krypton or xenon in the cases of Figs. 2 and 3 as indicated in the figures, and were 6 keV argon in the case of Fig. 4. The left-hand side pictures in Figs. 2 and 3 are patterns obtained from a basal plane of zinc, *i.e.* a single crystal of zinc with a face of basal plane is placed in such a way as the crystal face of basal plane will be bombarded by the incident ion beam. All the patterns shown in this paper were obtained by normal incidence of ion beam. Oblique incidences were also used, although they are not shown in this paper*.

The pattern from the basal plane of zinc shows a precisely equilateral hexagonal deposit. The direction of a-axis of the crystal is shown in the figures. The patterns from prismatic planes, *i.e.* $(10\bar{1}0)$ and $(11\bar{2}0)$, are shown in Figs. 2 and 3. The $(10\bar{1}0)$ pattern is an indistinct polygon, and the $(11\bar{2}0)$

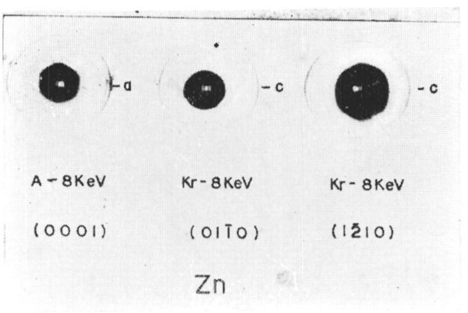

Fig. 2. Sputtering deposit patterns from various planes of zinc crystal. (Faint thorn-like figures which may be visible along the peripheries of deposit patterns are the trace of meshes of section paper used as the background of the picture. They have nothing to do with the deposit patterns, of course.)

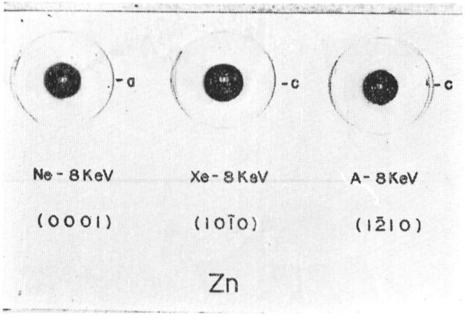

Fig. 3. Sputtering deposit patterns from various planes of zinc crystal. (Faint thorn-like figures which may be visible along the peripheries of deposit patterns are the trace of meshes of section paper used as the background of the picture. They have nothing to do with the deposit patterns, of course.)

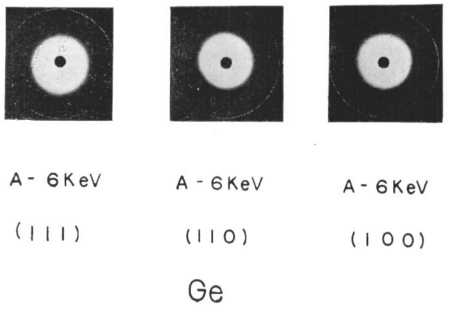

Fig. 4. Sputtering deposit patterns from various planes of germanium crystal.

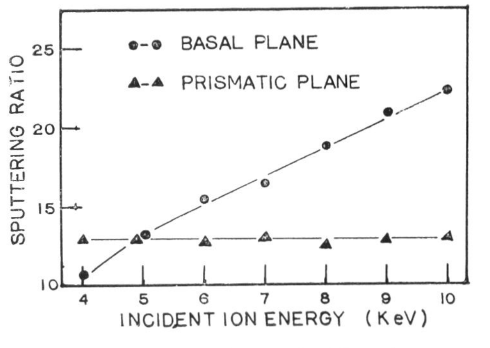

Fig. 5. Sputtering ratios *vs* incident ion energy. Probable error in the measurements of sputtering ratios is about ±1.

* Angular dependence of sputtering ratios and of deposit patterns will be described later elsewhere.

pattern is a somewhat distorted hexagon. The direction of c-axis of the crystal is indicated in the figures.

The sputtering ratios as a function of incident ion energy are shown in Fig. 5 for atom ejections from the basal plane and the prismatic $(10\bar{1}0)$ plane. The behaviors are quite different in these two planes.

Sputterings from various planes of germanium crystals always form circular deposits. The patterns from (111), (110) and (100) planes are shown in Fig. 4, in which black and white are reversed. These circular deposits mean that atom ejections from all these three planes are isotropic.

4. Discussions

The equilateral hexagonal pattern from the basal plane of zinc crystal cannot be understood by the focused collision of atoms along the close-packed atomic row, which lies only in the basal plane. It is found from the pattern that the direction of the ejection of atoms is $\langle 20\bar{2}3\rangle$, which is one of the directions which connect the nearest neighbor atoms.

The atomic arrangement in $\langle 20\bar{2}3\rangle$ direction is shown in Fig. 6. Open circles show atoms, which make couples of nearest neighbors. No atom is found at crossed positions. Therefore, it is impossible for a focused collision in usual sense to occur.

Now we shall consider two atoms, which are nearest neighbors with each other, at the crystal surface of (0001) plane (Figs. 6 and 7). The atom 1 in Fig. 7 is hit, for example, by a knocked-on atom as shown in the figure. Then the atom 1 will hit the atom 2. Now, if

$$\theta_1 > \theta_2 ,$$

there will be a tendency of focusing which produces a focused deposit pattern. But this is not usual chain of focused collision. We shall call this a "single event focusing". If the single event focusing is effective at the (0001) surface, the equilateral hexagonal deposit pattern is expected.

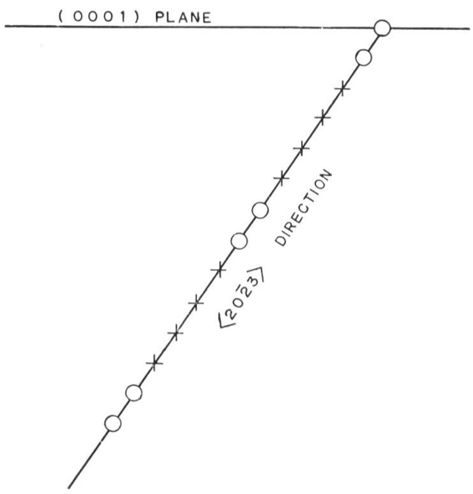

Fig. 6. Atomic arrangement in $<20\bar{2}3>$ direction in zinc crystal.

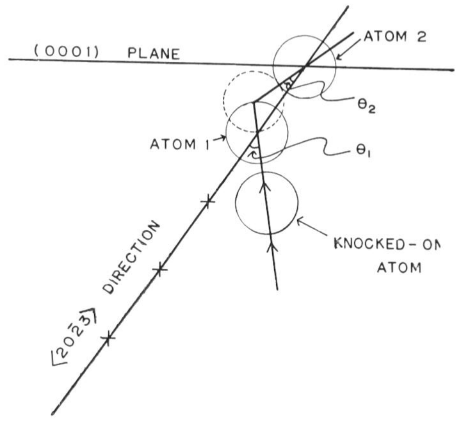

Fig. 7. "Single event focusing" in $<20\bar{2}3>$ direction in zinc crystal.

Another possible interpretation is that there may occur a complex (or three dimensional) focused collision, if the surrounding atoms help it. This kind of complex focused collision is found in $\langle 100\rangle$ collision in copper[3]. If only one dimensional array of atoms is considered, $\langle 100\rangle$ chain of collision cannot occur in copper. But it does occur, because surrounding atoms assist it in the three dimensional crystal. We do not know at present if this kind of three dimensional focusing collision does occur in $\langle 20\bar{2}3\rangle$ direction in zinc crystal. It will be worthwhile to make machine computation to verify the possibility of $\langle 20\bar{2}3\rangle$ focusing*.

The deposit patterns from prismatic planes of zinc crystal again cannot be explained by the focused collision chain in usual sense only, although we cannot rule out it (Figs.

* This was suggested by Dr. G. H. Vineyard in private conversation during the International Conference on Crystal Lattice Defects, Tokyo and Kyoto, 1962.

2 and 3). Some part of the pattern may be due to the usual focused collision, but there is no sign that the deposits in the usual focusing directions are predominant. The deposits in directions other than usual focusing directions must be again explained either by "single event focusing" or "three dimensional focusing".

The sputtering ratio is higher in the basal plane sputtering as compared with that of the $(10\bar{1}0)$ prismatic plane sputtering in the energy range of our interest, as are shown in Fig. 5. A qualitative explanation for this can be easily given. As the density of atoms in the basal plane is higher than that in the prismatic plane, the collisions occur in the vicinity of surface more in the case of basal plane surface than in the case of prismatic plane surface. This results in a higher sputtering ratio in the basal plane sputtering*.

The high sputtering ratio in the basal plane sputtering seems to be disadvantageous for the view that the focused chain collision in usual sense is predominant. Because if the focused chain collision is predominant, the sputtering ratio should be higher in the prismatic plane sputtering, but actually this is not the case.

It may be concluded in the case of zinc crystal that the focused collision in usual sense along close-packed atomic rows is not the most predominant collision event, although its existence cannot be ruled out. We have to consider a "single event focusing" or a "three dimensional focusing" to explain whole the deposit patterns.

Now in the case of germanium, the deposits from various planes show always homogeneous isotropic circular patterns. This shows that no focused collision nor "single event focusing" takes place in germanium. This is understandable, if we consider the collision diameter of germanium atoms (or rather germanium ions): *i.e.* the diameter of knocked-on germanium atoms at the moment of collision is considered to be very small compared with the distance between two neighboring atoms. This situation should result in an isotropic sputtering.

It should be recalled that the collision diameter changes as a function of the energy of incident atom. Therefore, it is possible that an anisotropic deposit pattern will be obtained in the low energy sputtering experiment, because the collision diameter of atom will become larger, when the energy of incident atom becomes smaller. This is actually the case, and Anderson and Wehner[4] observed anisotropic patterns of germanium in a low energy range.

In the case of germanium, it may be concluded that no focusing occurs as far as the energy of our interest is concerned, and that this is explained by the small collision diameter.

Acknowledgement

The authors are indebted to Dr. S. Okuda, who constructed the experimental facilities in the beginning of the series of our sputtering experiments.

References

1 R. S. Nelson and M. W. Thompson: Proc. Roy. Soc. A, **259** (1961) 458.
2 F. Keywell: Phys. Rev. **97** (1955) 1611.
3 J. B. Gibson, A. N. Goland, M. Milgram and G. H. Vineyard: Phys. Rev. **120** (1960) 1229.
4 G. S. Anderson and G. K. Wehner: J. Appl. Phys. **31** (1960) 2305.

DISCUSSION

Schmid, E.: I would like to give a short comment. We also tried to prove the question of focusing collisions in Zn-crystals using single crystal wires of different orientations, c-axis being parallel and normal to the wire axis. The crystals were irradiated by α-rays and the electrical resistivity was measured as a function of the dose. The results could de understood by the existence of focusing collisions in the most densely packed direction.

Bragg, R. H.: Your photographs for germanium appear very much like x-ray powder photographs or powder photographs superimposed with Laue patterns. Could this be due to the fact that your surfaces were really polycrystalline instead

* The energy dependence of sputtering ratio and the collision processes will be discussed later elsewhere.

of single crystal? Did you etch them?

Hasiguti, R. R.: Our germanium crystals were supplied by Toshiba Electric Co., where specialists make really good single crystals. We do not think the crystal surface became polycrystalline during bombardment, because the same experimental arrangement gives anisotropic patterns in the cases of silver and zinc. We have never etched chemically, but sputtering itself has an etching effect. As far as the surface etched by sputtering is observed by light microscope, there is no sign of polycrystalline structure.

Müller, E. W.: Cathode sputtering damages the crystal structure in the surface. I should like to know the sputtering rates, or the current density of the sputtering ions. It is very important for ejection patterns to have a clean and smooth surface.

Hasiguti, R. R.: Typical current density in our experiment is $1 \sim 3$ A/mm^2. I think that ion irradiation damages the crystal in the surface layer in the sense that lattice defects are produced in it. But I do not think the crystal structure is completely destroyed.

Brandon, D. G.: I think Professor Müller's point is that the considerable disturbance produced by ion bombardment and observed directly in the field ion microscope essentially destroy the single crystal structure of the surface. Direct transmission examination of ion bombarded metal films in the electron microscope shows that this is not the case. Although the Kikuchi line pattern is destroyed by the very high density of defects introduced, the diffraction spot pattern is retained and no diffuse rings are observed.

Gonser, U.: Recent experiments at Aachen (T. Ric, W. Sibley) give indication of correlated collision processes of b.c.c. Ta and KBr by deuteron bombardment and sputtering. In the case of KBr the sputtered atoms from the surface are predominantly Br atoms.