THRESHOLD OF DAMAGE BY XENON IONS IN GOLD AND SILVER

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Summary

Gold and silver crystals have been bombarded with xenon ions and the minimum ion energy E_t that causes damage has been measured. This threshold depends on the orientation of the crystal in a manner that is consistent with a damage mechanism in which energy is directed along $\langle 110\rangle$ directions. For gold $E_t^{110} = 16\cdot 5$ eV, $E_t^{111} = 20\cdot 5$ eV, and $E_t^{100} = 23\cdot 5$ eV, while for silver all values are 1 eV less. The accuracy is $\pm 0\cdot 5$ eV. The relationship of these values to those obtained for damage of metals by electron bombardment is examined.

I. Introduction

When an inert gas ion of low energy is incident on a metal surface, it is neutralized just before it reaches the surface (Hagstrum 1954*a*, 1954*b*) and then transfers its momentum to the atoms of the metal crystal by predominantly elastic collisions (Bohr 1948). This may cause metal atoms to be permanently displaced, with resulting damage if they stay within the crystal and sputtering if they are ejected from it.

If a metal foil is bombarded with ions and subsequently examined in an electron microscope, a high density of dislocation loops and lines is usually found in the bombarded area. This damage has been studied most extensively in gold (Bowden and Brandon 1961; Brandon and Bowden 1963; Ogilvie, Sanders, and Thomson 1963; Venables and Baluffi 1965*a*, 1965*b*; Thomas and Baluffi 1967), where the damage is apparently caused by atoms initially displaced into interstitial positions in the crystal aggregating to form the visible dislocations.

For gold foils bombarded with singly charged ions of an inert gas, Ogilvie, Sanders, and Thomson (1963) determined directly the ion energy E_t at the threshold of damage. The ions were directed perpendicular to a (111) plane and it was shown that E_t varied with the mass of the ion. From the measured values of E_t, the maximum part of the energy of the ions, ρE_t (where $\rho = 4m_1 m_2(m_1+m_2)^{-2}$ and m_1 and m_2 are the masses of the ion and atom respectively), which could be transferred to an atom in the crystal was determined. The values of ρE_t for neon, argon, and xenon ions were the same within experimental error and close to 20 eV for ions normal to a (111) plane.

Damage may also be produced by electron bombardment, and this effect has been studied extensively by measuring the electrical conductivity of copper foils (Eggen and Laubenstein 1955; Corbett and Walker 1960; Lucasson and Walker 1962; Sosin 1962; Bauer and Sosin 1964*a*, 1964*b*; Kamada, Kazumata, and Suda 1964). An objective of these studies has been to determine T_d, the minimum energy required to cause the permanent displacement of an atom from its lattice site in

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the crystal, and values between 19 and 30 eV have been obtained. Huntington (1954) estimated theoretically the minimum energies required for a copper atom to be permanently displaced in different low-index directions and found values of 18·5 eV in the ⟨111⟩ and 17·5 eV in the ⟨100⟩ directions. Using an iterative procedure, Gibson *et al.* (1960) made detailed calculations of the spread of momentum from a recoiling atom in a face-centred cubic crystal model representing copper. Among the results of this study were values of the angular dependence of the displacement threshold. They found 24, 28, and 85 eV in the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions respectively. The threshold E_{t}^{hkl} is clearly related to the minimum energy E_{min}^{hkl} that must be given to a surface atom by impact to cause a permanently displaced atom to appear in the crystal. On general grounds E_{min}^{hkl} is roughly equal to T_{d}^{hkl}, the minimum energy required by an atom similarly struck within the crystal to produce a similarly displaced atom, and is roughly 1 eV less than T_{d}^{hkl}. In view of discrepancies in the measurement of T_{d} by electron bombardment, and the demonstration that E_{t} can be measured to better than 1 eV, it seemed important to determine the nature of the angular dependence of E_{t}. Consequently, values of E_{t} have been obtained in [111], [110], and [100] directions in silver and gold specimens using xenon ions, as Ogilvie, Sanders, and Thomson (1963) showed that damage thresholds were most clearly defined when these ions were used. An attempt to make similar measurements with copper was not successful.

II. Experimental Procedure

(a) *Specimen Preparation*

Gold and silver crystals with (100), (111), or (110) planes in the foil plane were grown by condensation on heated NaCl crystals cleaved or cut to expose these planes. Crystals with (100) faces were used as cleaved. For the other orientations the (110) crystals were sawn appropriately and etched in distilled water for (110) faces or in water nearly saturated in NaCl and urea for (111) faces. The etching process was abruptly terminated by flooding the crystal with methyl chloroform.

The evaporations were made in a baked all-glass system in order to minimize contamination of the condensed metal films. The metal charge was of high purity (better than 99·999%). The evaporation apparatus is shown in Figure 1. Its pumping system was oil free, the mercury diffusion pump being backed by a stainless steel automatic mercury piston pump (Davis and Ogilvie 1966) with multiple cold traps. The cold trap adjacent to the apparatus was baked with it to 400°C prior to chilling.

Since (100) films of gold could not be formed without prior ion bombardment of the substrate, the following procedure was used as a standard for all orientations. The pressure in the system was reduced to less than 10^{-7} torr, and xenon was then admitted to a pressure of 2×10^{-4} torr. With magnetic field and potentials as shown in Figure 1, a gas discharge was established. When a 10 MHz r.f. power supply was connected to the crystal holder as shown, Xe^{+} ions were then able to bombard the NaCl surface (Anderson, Mayer, and Wehner 1962). At the end of the ion bombardment, the zenon was pumped away and the metal film condensed to the desired thickness on the NaCl crystal maintained at 270°C.

(b) *Ion Bombardment*

The experimental discharge tubes were as described by Ogilvie, Sanders, and Thomson (1963), except for the use of a hydrocarbon-free vacuum system. The source of ions was a low pressure non-self-sustaining arc discharge between a unipotential oxide-coated cathode and a nickel anode. The metal foil specimen was mounted on an electron microscope grid and enclosed in a capsule of the same material. A window in the capsule allowed ions to bombard part of the specimen. The capsule was supported in the discharge plasma and ions were accelerated normal to its surface with an energy determined by the potential difference between the specimen and the plasma, the potential of which was continuously monitored with a Langmuir probe. The ion energy was defined by this method to better than $\pm 0\cdot 5$ eV, the principal uncertainty being the contact potential difference (c.p.d.) between specimen and cathode.

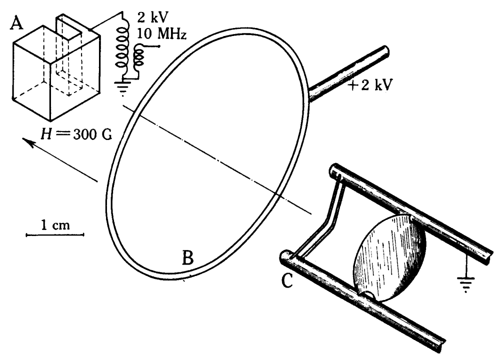

Fig. 1.—Schematic arrangement of evaporation apparatus:
A, Crystal support heated by a filament immersed in the slot of the stainless steel block. The NaCl crystal plate is clamped against the opposite face to the slot. The temperature of the block is measured with a thermocouple.
B, Nickel wire anode ring.
C, Evaporation filament. The purpose of the plate, made of nickel, is to increase the discharge current.

The magnitude of this c.p.d. was assessed by the diode method in which the currents drawn by anode and specimen in turn from the hot cathode with all other electrodes connected together were measured as their potential was varied through values insufficient to excite a gas discharge. The correction for the c.p.d. inferred from these results was smaller than the experimental error and did not exceed $0\cdot 2$ eV. This unexpectedly low value of the c.p.d. may be due to the transfer of metal from the edges of the specimen capsule on to the anode by a sputtering mechanism during processing. It is known (Wehner 1954) that ions arrive with small angles of incidence at the edges of a conducting plate inserted in a plasma and that these ions are very effective in ejecting atoms, doing so at much lower energies than ions normally incident on the surface.

(c) *Threshold Measurement*

Each specimen was bombarded with ions to a total dose of at least 10^{19} ions cm^{-2} while the discharge apparatus was immersed in a dry ice–acetone bath to inhibit specimen annealing. At the end of the bombardment the tube was cut open and the specimen on its grid was extracted and inserted in an electron microscope. Comparison between adjacent bombarded and unbombarded areas of the same specimen was used to determine whether damage had taken place. Each tube was run at a different ion energy until a value E_t of this energy was found such that for energies $0 \cdot 5$ eV above it clearly visible damage resulted, whilst for energies $0 \cdot 5$ eV below it there was no trace of such damage.

III. Results

The experimental results are summarized below.

	Gold			Silver		
Orientation of film	110	111	100	110	111	100
Threshold E_t (eV)	16·5	20·5	23·5	15·5	19·5	22·5

An attempt to make similar measurements for copper failed because, in areas of the specimens that were not bombarded after processing in the experimental tubes, the defect concentration was so high that an accurate measurement of the threshold could not be made. However, damage was clearly visible in copper specimens bombarded with ions having energies $\geqslant 19$ eV when the ions were directed in a [110] direction.

IV. Discussion

The experiments show that the threshold of damage depends on the direction in which the ions are incident, the smallest value occurring when the ions are directed along [110]. Of the various processes that have been suggested to explain displacement of atoms by irradiation, the only one predicting an orientation dependence of the type found in these experiments is the focused collision sequence along $\langle 110 \rangle$ (Silsbee 1957; Gibson *et al.* 1960; Nelson and Thompson 1961). Elementary mechanics shows that the energy E_s transferred to a surface atom by an ion of energy E_i is given by

$$E_s = E_i \cos^2\phi \, 4m_1 m_2(m_1+m_2)^{-2},$$

where ϕ is the angle between the direction of incidence of the ion and the direction in which the atom recoils, and m_1 and m_2 are the masses of the ion and atom respectively.

If the energy E_i of the incident ions is increased from zero there will be a value above which the resulting collision sequence causes a displaced atom to appear interstitially within the crystal. This energy depends on the angle between the directions of recoil of the first atom in the sequence and the collision sequence initiated by that recoil, but the manner of the dependence is as yet unknown. However, the minimum energy E_{min} that must be given to the first atom in the collision sequence to produce a displaced atom will have its least value when $\theta = 0$, i.e. the first atom recoils in a close packed direction. Therefore, when ions with energy $E_i = E_t^{110}$ are incident in this direction, only those collisions between ion and surface atom with impact parameter equal to zero (i.e. head-on collision) initiate collision sequences resulting in damage, and because $\phi = 0$ in this case

$$E_s = E_{min} = 4\, m_1 m_2(m_1+m_2)^{-2} E_t^{110}.$$

By making the reasonable assumption that E_{min} is determined by the value of θ alone for any plane in the [110] zone (in hard sphere models this is valid for $\theta < 30°$), the angular dependence of $E_{\min}$ over a limited range of θ can be inferred from the measured values of E_t^{hkl} because the directions of ion incidence, the resulting collision sequence, and the recoil of the first atom in that sequence all lie in the same plane when $E_i = E_t^{hkl}$, as demonstrated in Figure 2. The curves expressing the angular dependence of $E_{\min}$ and E_s, when the ions are directed along [*hkl*] and $E_i = E_t^{hkl}$, are clearly tangential (if they intersected there would be a range of values of $E_s(\theta) > E_{\min}(\theta)$, implying that $E_i > E_t$) and this fact can be used to construct a curve showing the angular dependence of $E_{\min}$ as shown in Figure 3 for gold. The curve for silver is nearly the same with all values about 1 eV less.

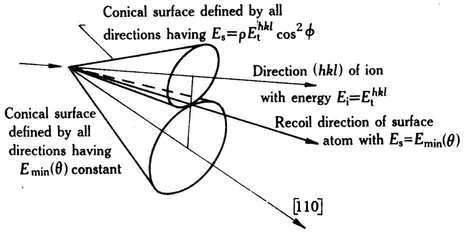

Fig. 2.—Geometry of recoil of a surface atom that initiates a collision sequence along [110] producing an interstitial atom within the crystal.

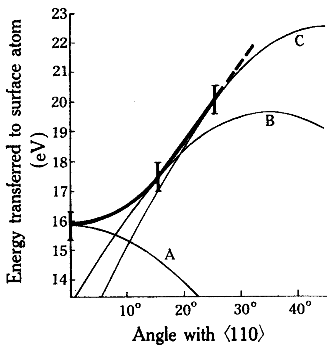

Fig. 3.—Angular variation of the threshold of displacement, $E_{\min}(\theta)$, by focused collision sequences in gold. This curve is tangential to the curves A, B, and C of $\rho E_t^{hkl}\cos^2\alpha$, where α is the angle made with the [*hkl*] directions [110], [111], and [100] respectively.

For some time it has been thought that the fact that atoms tend to be ejected from a crystal in ⟨110⟩ directions during ion bombardment verified experimentally the operation of focused collision sequences along ⟨110⟩ in radiation damage. However, Harrison, Johnson, and Levy (1966), after a computer simulation of the sputtering process in copper, concluded that such sequences were not necessary to explain the experimental results. Lehmann and Sigmund (1966) and Olsen and Smith (1967) have come to essentially the same conclusion. On the other hand, Nelson and von Jan (1968) deduced from their calculations that ⟨110⟩ collision sequences must play a major part in the ejection process. In addition, Thompson (1968), from an analysis of the energy spectrum of atoms sputtered from a gold crystal, obtained evidence for this conclusion. Thus there is at present an uncertainty about the role of ⟨110⟩ collision sequences in sputtering. However, there is not the same doubt in the case of radiation damage and the results presented in this paper appear to demonstrate experimentally that damage is due to focused collision sequences alone when E_s is close to $E_{\min}$.

The interpretation of the experimental results given above yields threshold values that do not agree with those obtained from electron bombardment experiments. The curve expressing the relationship of electron energy to the resulting resistivity change produced by bombardment usually has a stepped appearance and is considered to be the sum of two components each with a different threshold. The component with the lower energy threshold has been associated with indirect displacement processes involving light atom impurities and the other component with direct displacement (Bauer and Sosin 1964*a*). This interpretation led to the following values of T_d for gold: > 40 eV (Lucasson and Walker 1962), near 40 eV (Minnix and Shearin 1963), and 33–36 eV (Bauer and Sosin 1964*a*). Similar measurements for copper have given: 19 eV (Sosin 1962), 16–19 eV (Bauer and Sosin 1964*a*), and 28–30 eV (Kamada, Kazumata, and Suda 1964). A value for silver of 28 eV has been given by Lucasson and Walker (1962). It is only in the case of copper that a search for a directional dependence of T_d has been made and this experiment gave $T_d^{100} = T_d^{111} \simeq 19$ eV (Sosin and Garr 1965).

Bauer and Sosin (1964*a*) calculated the cross sections of a number of indirect displacement processes and they were able to get good agreement between the results of electron bombardment experiments made with copper doped with beryllium and their calculations. However, they showed that the calculated cross sections for indirect displacements were too low to account for the observed resistivity changes below the high energy threshold for pure copper. It is therefore not entirely unreasonable to propose that the lower of the two thresholds is due to a direct rather than an indirect displacement mechanism. This threshold for gold was found to be 15 eV by Bauer and Sosin (1964*a*) and because the value was obtained for polycrystalline specimens this is equivalent to $T_d^{110} = 15$ eV, as only the most favourably oriented crystals would have atoms displaced within them. The ion bombardment threshold for gold is very close to this value (and is equivalent to $T_d^{110} \simeq 17$ eV).

It is relevant to note here that indirect displacement of atoms in gold and silver specimens will not take place by the mechanisms proposed by Bauer and Sosin because the mass of the xenon ion is similar to the mass of gold and silver atoms. The agreement between the lower electron bombardment and the ion bombardment thresholds makes it likely that the same displacement mechanism, i.e. collision chains directed along $\langle 110 \rangle$, operates in both bombardments.

It is implied by the above considerations that a new meaning has to be assigned to the upper electron bombardment threshold. The most likely possibility is the onset of damage caused by collision sequences directed along $\langle 100 \rangle$ for which calculations have been made by Nelson and Thompson (1961). Although the computed threshold is more than twice the experimental value, this discrepancy could easily be caused by the approximations used in the calculation. Furthermore the results of unpublished calculations by Erginsoy and Thompson (quoted from Thompson 1968) are consistent with this interpretation, They found that the energy loss in the first replacement in a collision sequence directed along a $\langle 100 \rangle$ direction in gold is about 30 eV and this value is close to the experimental upper threshold of 33–36 eV obtained by Bauer and Sosin (1964*a*).

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