Damage Clusters in Molecular-Ion-Bombarded Gold Observed by Transmission Electron Microscopy

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(Received 17 February 1976)

Stereo electron microscopy of gold bombarded at room temperature with atomic and molecular ions shows that the nature of damage clusters is sensitive to the density of deposited energy. Both the total number of defects and their distribution in space show that vacancy loops are formed preferentially at high density of deposited energy and interstitial loops at low density. Calculations indicate that the limiting density corresponds to $\sim 10^{-2}$ point defects per atom.

Bombardment of metal foils with heavy ions at keV and higher energies produces radiation damage that is often visible with use of an electron microscope. For gold bombarded at room temperature, it has been established that in the 10–500-keV region, about one visible change cluster is produced for each incident ion.[1] This result, as well as the size[2] and depth[3,4] distribution of the observed damage clusters, suggests that the individual cluster (and its location in space) is determined primarily by the energy deposition of the individual bombarding ion. A close correlation between calculated energy deposition profiles[5] and observed depth distributions of damage clusters has been shown recently for a series of ions in the energy range 50–150 keV implanted into gold at room temperature.[4] The nature of the defects was also determined in that work: The relative abundance of vacancy and interstitial loops was found to depend essentially on the mass (or atomic number) of the bombarding ions. Up to mass number 83 (Ar, K, Fe, and Kr), a majority of interstitial loops were produced, while heavier ions (Rb, Mo, Yb, Xe, and Au) produced mostly vacancy loops. The chemical nature and radius of the implanted species had no visible effect on the nature of the damage, which was conjectured to be determined essentially by the deposited energy density and the defect mobility at the bombardment temperature. The importance of defect mobility was demonstrated experimentally in Ref. 4; in this Letter, we report an experiment that was performed in order to confirm the key role of the deposited energy density.[6]

It is well known[5] that for a given target and implantation energy, an increase in the projectile mass produces a decrease in its penetration depth and in the size of the damaged region. This increases the density of deposited energy (energy per atom) by almost three orders of magnitude when the projectile mass varies from Ar to Au.[6] In order to vary the deposited energy density without changing the penetration depth and the chemical nature of the ion, we have compared gold foils bombarded by atomic and molecular ions with identical velocities. This technique has recently been introduced to study the mechanism of sputtering[7] and of ion-bombardment damage in silicon.[8]

Although incoming molecules have a high probability of dissociating immediately upon entering the surface, the trajectories of the constituent atoms are correlated in the initial portions of the path. The correlation gradually disappears because the ions are scattered. For example, the ion path length of As ions in gold is about twice the average projected range,[5] so that the

energy deposition is increased (and the two damage cascades overlap) up to a depth of roughly half the projected range. Beyond that depth, the damage is expected to be increasingly determined by the energy deposited independently by the two projectile atoms.[9]

Room-temperature implantation of 55-keV As^{2+},[10] 110-keV As_2^+, and 80-keV $AsCl^+$ ions were performed into prethinned Au foils (99.99% purity) with the Orsay ion implanter.[11] This corresponds to 55 keV per As atom. The beam current was about 2×10^{10} (ions/cm^2)/sec, and total doses were about 3×10^{11} ions/cm^2 in all cases. The depth and nature of the damage clusters were measured by a standard stereoscopic technique[12] with a 100-keV transmission electron microscope. The error on the depth is typically 15 Å; the observed cluster sizes lie between ~20 Å and ~150 Å (the minimum observable diameter in such experiments is ~10 Å). Since the clusters are small, their nature is determined by the black-white (B-W) contrast under dynamical two-beam conditions in dark-field micrographs. As is well-known,[3,12] the strain contrast of these small clusters then depends on the nature of the sample and on the diffraction vector $\vec{g}$: The effect of these parameters is described by a characteristic "extinction distance" ξ_g (e.g., for Au, $\xi_g = 230$ Å for $\vec{g} = \langle 220 \rangle$). For such small clusters, the strain contrast is always along $\vec{g}$. In our experiments, the clusters are all identified as dislocation loops (from the variation of the contrast with $\vec{g}$). No three-dimensional clusters (such as tetrahedra) were observed. The direction of the B-W contrast along $\vec{g}$ depends both on the nature of the clusters and on their distance h from the surface, as long as $h < \frac{5}{4}\xi_g$. Vacancy loops produce a B-W contrast for $h < \frac{1}{4}\xi_g$ and $\frac{3}{4}\xi_g < h < \frac{5}{4}\xi_g$; the contrast is W-B if $\frac{1}{4}\xi_g < h < \frac{3}{4}\xi_g$. Interstitial loops produce contrasts opposite to those of vacancy loops. The sensitivity of the technique is identical for both types of loops. Beyond $h = \frac{5}{4}\xi_g$, the contrasts are symmetrical, and the nature of the small clusters can no longer be identified. This technique is, however, unfavorable for cluster size and density measurements; hence, only qualitative information was obtained on those parameters.

Figure 1 shows the depth distributions of vacancy loops (above the scale) and interstitial loops (below the scale) for the three bombarding ions. The fraction of interstitial clusters is seen to drop from 0.90 in the case of arsenic ions (Fig. 1, *a*) to 0.40 and 0.35, respectively, for AsCl and As_2 ions (Fig. 1, *b* and *c*). Moreover, Fig. 1 shows that where the correlated damage cascades overlap (i.e., near the surface), the probability of creating a visible vacancy cluster increases markedly (compare *a* and *c*). It may be argued that trapping of interstitials by the surface should favor vacancy-cluster (over interstitial-cluster) formation. This effect certainly occurs, but it should not be different for As- and As_2-implanted samples. Moreover, after implantation of other light ions,[4] interstitial clusters were found very close to the surface (~30 Å). Hence, surface trapping of interstitials cannot account for the large difference in the vacancy loop distributions of Fig. 1.

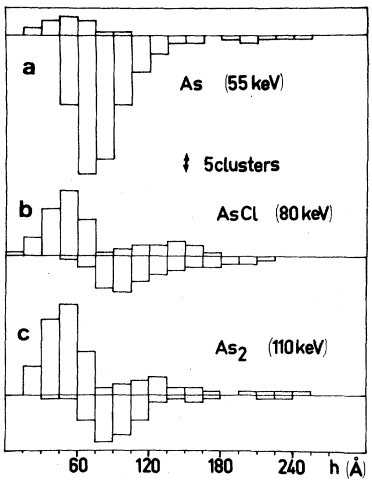

FIG. 1. Nature and depth distributions of damage clusters for As^{++}, $AsCl^+$, and As_2^+ implanted into Au at room temperature. The energy is 55 keV per As atom in all cases. Beam currents and total doses (3×10^{11} ions/cm^2) are the same in all cases. Vacancies above scale; interstitials below scale.

Figure 2 shows depth distributions of clusters regardless of their nature. For atomic arsenic (Fig. 2, *a*), the profile has a maximum at depth 60–75 Å, and a mean depth very close to the theoretical value[5] $\langle x \rangle_D = 90$ Å of the average energy-deposition depth. The profile is narrower than the theoretical energy-deposition profile ($\langle \Delta x^2 \rangle_D / \langle x \rangle_D^2 = 0.5$ for the relative damage straggling[5]). This is expected[13] because the measured profiles are deduced from the centers of observed dislocation loops (regardless of their size) rather than by estimating the total damage at any given depth. In the case of $AsCl^+$ and As_2^+, the maximum of the distribution has shifted somewhat towards the surface. Figure 1 shows that this shift is caused by the enhanced production of vacancy

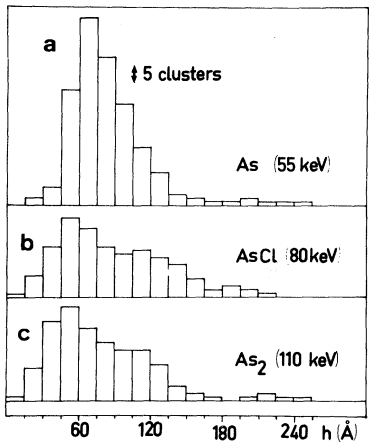

FIG. 2. Depth distribution of damage clusters regardless of their nature. The total number of clusters is larger than the sum of vacancy and interstitial loops in Fig. 1, because identification was impossible for up to 25% of the observed clusters.

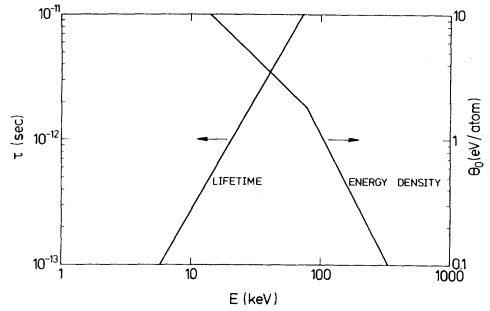

FIG. 3. Energy density θ_0 and time constant τ versus ion energy E for gold bombarded with atomic arsenic ions, according to Ref. 6.

loops, while interstitials are observed predominantly at larger depths.

In order to understand the strong apparent influence of energy deposition density on the nature of the damage clusters, we first consider Fig. 3, which shows the calculated energy density θ_0 (energy per atom) in the center of the damage cascade for atomic arsenic incident on gold, evaluated within the scheme of Ref. 6. At 55 keV, we have $\theta_0 \sim 2.5$ eV/atom. This is equivalent to a primary defect concentration of $\sim 1\%$ per atom, so that point-defect saturation phenomena are important. Enhancing the energy density by a factor ~ 2 via mere overlap of cascades increases the size of the region with such high-energy deposition. This situation should lead to immediate recombination of single defects, unless some separation occurs between vacancies and interstitials.

Figure 3 also shows the time constant τ, i.e., the time within which the peak deposited energy density drops[6] from θ_0 to $\theta_0/2$. At 55 keV, τ is of the order of 10^{-11} sec, much longer than the slowing-down time of the ion ($\sim 10^{-13}$ sec), so that spike phenomena must play a role. During the spike decay, energy is transported preferentially from the inner to the outer regions of a cascade[6]; some particle transport must accompany energy transport, thus leading to an excess concentration of vacancies in the center of the cascade. Hence, in the primary damage state some degree of separation of vacancies from interstitials does occur (Seeger zones[14]). The same effect causes exceptionally high sputtering of gold under similar bombardment conditions.[7]

The type of defect cluster that is formed then results from the competition between defect mobility and deposited energy density. At room temperature, interstitials are extremely mobile in gold while vacancy mobility is low. Figure 1 shows that in the heart of the primary cascade the deposited energy density is large enough to nucleate a vacancy cluster; in the deeper part of the penetration profile, where this condition is not satisfied, migrating interstitials nucleate interstitial clusters. Higher vacancy mobility can apparently compensate for reduced vacancy concentration (i.e., deposited energy density); this shows up in an increased probability of vacancy-cluster formation when the sample temperature is raised.[4]

Several points remain unsettled in this discussion: (i) The effect of the defect mobility is very strong[4] and warrants further study. (ii) According to Ref. 6, the energy density θ_0 is expected to depend on ion *energy* and not only on mass: θ_0 should *decrease* with *increasing* ion energy. Thus, for the heavier ions, one expects a relative increase in the number of interstitial loops with increasing ion energy. This effect has not been found in previous work,[4] but a systematic search has not been carried out yet. (iii) The effect of host impurities on the nature of defect clusters is presently under study. (iv) Finally, we wish to stress that our experimental results do not allow direct conclusions on the *total* damage production in gold by atomic- versus molecular-ion bombardment, since only sufficiently large defect clusters ($\gtrsim 20$ Å) are visible with use of the electron microscope.

We wish to thank F. Lalu and M. Salome for their assistance in the ion implantations.

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Superfluidity of Periodic Solids

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(Received 8 December 1975)

Leggett's investigation of the superfluid density of solids has been extended. By employing plane waves as a basis set, one can obtain the superfluid fraction ρ_s/ρ_0 as a function of the localization parameter. Solid He^4 is estimated to have a ρ_s/ρ_0 between 0.05 and 0.2 at zero temperature. This approach also sheds light on the superfluidity of thin films and the "index of refraction" of fourth-sound chambers.

In 1970, Leggett considered the possible superfluidity of solids.[1] Analyzing only temperature $T=0$, he observed that if a modified crystal wave function [obtained by letting all single-particle states develop a phase $\varphi(\vec{r})$] were stable with respect to the decay of excitations (the Landau criterion[2]), then one can define a meaningful superfluid fraction ρ_s/ρ_0, where ρ_s and ρ_0 are the superfluid and average number densities. Observation of the moment of inertia of a macroscopically large rotating annulus of height h, inner radius R, and thickness $d \ll R$ might thus yield a nonclassical moment of inertia (NCMI) I, where $I = (1-\rho_s/\rho_0)I_0$, and I_0 is the classical value. Leggett developed an expression giving a variational upper limit for ρ_s/ρ_0, but he did not evaluate it, instead relying on an analogy of this effect to the nuclear-exchange effect in solid He^3.[1] (Both effects disappear in the classical limit.) This led to an estimate of ρ_s/ρ_0 on the order of 10^{-4}, thus suggesting that the effect would not readily be observed at finite T.[3] Recently, Fernandez and Puma[4] evaluated Leggett's expression, finding for hcp He^4, the low temperature phase of solid He^4, that ρ_s/ρ_0 lies between 0.2 and 0.4. They then went on to argue that the ground-state wave function Ψ_0 probably does not possess off-diagonal long-range order,[5] and hence that it cannot describe superfluidity. However, their argument was not rigorous. Because of the unclear status