PHYSICAL REVIEW B VOLUME 16, NUMBER 9 1 NOVEMBER 1977

Radiation-annealing effects in energetic displacement cascades*

R. S. Averback and K. L. Merkle
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 16 May 1977)

Radiation-annealing effects due to energetic displacement cascades have been studied in copper, silver, and gold using electrical-resistivity measurements of thin-film specimens. It was found that close Frenkel pairs are unstable in the region of an energetic cascade. This was shown by doping the specimens with Frenkel pairs using a 150-keV proton irradiation at low temperature and measuring the damage rate during a subsequent heavy-ion irradiation. For ~ 500-keV self-ion irradiations the volume around the cascade in which close Frenkel pairs are unstable is 5×10^{-16}, 2×10^{-16}, and 4×10^{-17} cm^3 for silver, gold, and copper, respectively. Moreover, it was observed that the volume increased with increased energy density in the cascade. The implications of these results on defect production, defect saturation behavior, and isochronal recovery for damage produced in energetic cascades are discussed.

INTRODUCTION

Significant progress has been made in recent years in understanding both defect production in metals due to electron irradiations and the properties of the isolated vacancies and interstitials produced.[1] In energetic displacement cascades however, defect production and the interaction of the defects within the cascade are not nearly as well known, despite the technological importance of such information. For example, experimental values for the number of defects produced in energetic cascades are considerably lower than those from theoretical calculations.[2,3] Furthermore, the theoretical value for the saturation concentration of defects is higher for fast-neutron irradiations than for electron irradiations,[4-6] although this is not found experimentally; moreover, for copper and platinum the opposite has in fact been observed.[7-9] One mechanism that can qualitatively account for these observations is the possibility that close Frenkel pairs are produced in energetic displacement cascades but are unstable to recombination. Earlier self-ion bombardments gave indications that the energy density in cascades of silver and gold may be sufficiently high to anneal close pairs.[10] In addition, recent computer calculations have shown that the residual agitation in the lattice following the displacement spike induces close-pair recombinations in tungsten.[11] The present experiments show clearly that close pairs are in fact unstable in the vicinity of energetic cascades in copper, silver, and gold. A preliminary account of the present work has been presented in Ref. 12. The effective volume around each cascade in which recombinations take place is determined from the experimental results using a model for radiation annealing that includes stimulated close-pair (SCP) recovery.

To show the effect of energetic cascades on a preexisting population of Frenkel pairs, the following experiment was performed. First, specimens were doped with Frenkel pairs by irradiating with 150-keV protons below 10 K. This type of irradiation produces predominantly isolated Frenkel pairs and few clusters. When a given defect concentration was reached, the proton irradiation was terminated, and without warming the specimens were irradiated with energetic heavy ions (self-ions and other heavy particles). The change in electrical resistivity $\Delta\rho$ was measured during the irradiations as a function of ion dose ϕ. For specimens doped to a sufficiently high defect concentration, the resistivity decreased with dose at the beginning of the heavy-ion irradiation, indicating more defect annihilation than production [Figs. 1(a)–1(c)]. By comparing the damage rates $d\Delta\rho/d\phi$ of the doped and undoped specimens as a function of $\Delta\rho$, the number of doped-in Frenkel pairs recombining per incident ion was determined. That these differences between the damage rates were in fact due to close-pair recombinations was shown by repeating the experiment, but with the doping irradiation carried out at 50 K. In this case, the doped-in defects were produced similarly to those at low temperature, but, as the irradiation took place above stage I, close pairs were removed by thermal annealing. No reduction in the damage rate relative to the undoped specimen was observed upon subsequent heavy-ion irradiation for this doping treatment.

An experiment similar to the present one was performed by Brinkman and Gilbert in 1953.[13] In that study, thorium was irradiated to saturation with 9-MeV protons at 133 K. Subsequently, the specimen was irradiated with 18-MeV deuterons, also at 133 K. 18-MeV deuterons induce fission in thorium and as a result, the recoil spectrum

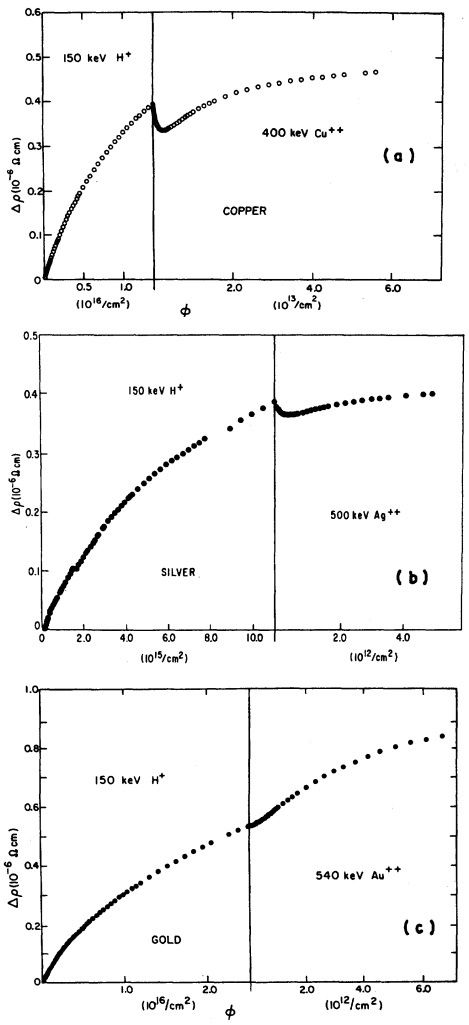

FIG. 1. (a) Resistivity change vs dose in copper. The first portion of the curve shows the resistivity change for a 150-keV proton irradiation below 10 K. The second portion shows the resistivity change for subsequent self-ion irradiation of the same specimen. (b) Same as (a) for silver. (c) Same as (a) for gold.

is on the average substantially higher in energy compared with that of a 9-MeV proton irradiation. Brinkman and Gilbert found that $\Delta\rho$ decreased upon deuteron bombardment of pure thorium but increased when a Au–3-at.%-Th alloy was irradiated. Since these irradiations were performed well above stage I (< 50 K in Th),[14] the observed reduction in resistivity upon deuteron bombardment cannot be due to the recombination of close pairs. Similar differences in the saturation behavior at 78 K between 1- and 2.9-MeV He^+-bombarded Au were, in fact, observed by one of us (K.L.M.). The saturation in radiation-induced resistivity at temperatures at which point defects are mobile is necessarily a rather complicated process, including effects from the kinetics of defect migration, cluster formation, trapping at impurities, and changes in the resistivity per point defect that occur due to the formation of large clusters at high doses. Although it may be argued that the reduction in induced resistivity upon introduction of more energetic cascades is likely to be due to the release of interstitials from impurities, the origin of the radiation annealing effects observed above stage I remains highly speculative.

In present work all damage-production measurements were performed at low temperature and therefore the complications that arise from kinetic effects do not have to be considered.

RADIATION-ANNEALING MODEL

The damage rate for irradiation with heavy ions is written

$$\frac{d\Delta\rho}{d\phi} = \left(\frac{d\Delta\rho}{d\phi}\right)_n - \left(\frac{d\Delta\rho}{d\phi}\right)_s . \tag{1}$$

The subscript n indicates the "normal" case of no doping, and s indicates the SCP recovery that occurs in the doped specimens. To a first approximation, the normal damage rate for energetic ions stopped within the specimen is given by

$$\left(\frac{d\Delta\rho}{d\phi}\right)_n = \rho_F \frac{N_F^c}{N_0 a}\left[1 - (C_i V_r + C_v V_r)\right] , \tag{2}$$

where ρ_F is the Frenkel-pair resistivity per unit concentration, N_F^c is the number of defects produced in the undamaged crystal by each ion, N_0 is the atomic concentration, a is the specimen thickness, C_i and C_v are the concentrations of interstitials and vacancies, respectively, and V_r is the spontaneous recombination volume for vacancies and interstitials.[6] $C_i V_r$ is therefore the probability that a newly produced vacancy is within the recombination volume of an already present interstitial, and $C_v V_r$ is the probability that a new interstitial is in the recombination volume of an old vacancy. Since $C_i = C_v = C$ and $\Delta\rho = \rho_F C$, the damage rate can be rewritten

$$\frac{d\Delta\rho}{d\phi} = \rho_F \frac{N_F^c}{N_0 a}\left(1 - \frac{2V_r}{\rho_F}\Delta\rho\right) . \tag{3}$$

Implicit in Eq. (3) is the assumption that the spontaneous recombination volume is independent of the defect concentration. For the present case, it is also assumed that the recombination volume per defect is the same for the Frenkel pairs produced by the proton irradiation as for those produced by the heavy-ion irradiation. These assumptions are not strictly valid,[9,15] however, for the purpose of evaluating SCP annealing; it is suffi-

cient that the "normal" damage rates be linear with defect concentration over a relatively short range of defect concentrations. This point will be discussed later.

SCP annealing is incorporated into the model by assuming all close pairs of concentration C_P recombine within a volume V_a around the cascade by SCP events. This assumption seems reasonable at least for silver and gold since recovery below 50 K, which is primarily due to close-pair recombination (i.e., substages I_A–I_D), is small for these metals after heavy-ion or fast-neutron irradiation.[16,17] The SCP annealing term is therefore

$$\left(\frac{d\Delta\rho}{d\phi}\right)_s = \rho_F \frac{C_P V_a}{a}\left(1-\frac{V_A}{V}\right), \tag{4}$$

where V_A is the total annealed volume in the specimen, and V is the total specimen volume. For a homogeneous defect distribution in the specimen, the fraction of the annealed volume is equal to the fraction of the annealed resistivity increment, i.e., $V_A/V = \Delta\rho_a/\Delta\rho_a^T$, where $\Delta\rho_a$ is the resistivity increment recovered during the irradiation due to SCP events and $\Delta\rho_a^T = \rho_F C_P$ represents the total resistivity increment from annealed close pairs. Equation (1) is rewritten

$$\frac{d\Delta\rho}{d\phi} = \rho_F \frac{N_F^e}{N_0 a}\left(1-\frac{2V_r}{\rho_F}\Delta\rho\right) - \rho_F \frac{C_P V_a}{a}\left(1-\frac{\Delta\rho_a}{\Delta\rho_a^T}\right). \tag{5}$$

Since the volume around a cascade in which SCP annealing occurs is presumably larger than the volume in which defects are produced, the second term in Eq. (5) is expected to go to zero faster than the first term. The quantities in the first term can therefore be obtained from the damage rates at high dose. The damage rates at low dose are then used to determine C_P and V_a. The close-pair concentration C_P is determined from

$$C_P = \frac{\Delta\rho_a^T}{\rho_F} = \frac{1}{\rho_F}\int_0^\infty d\phi \frac{d\Delta\rho}{d\phi} - \rho_F \frac{N_c}{N_0 a}\left(1-\frac{2V_r}{\rho_F}\Delta\rho\right), \tag{6}$$

and the annealing volume V_a is given by

$$V_a = \frac{[(d\Delta\rho/d\phi - d\Delta\rho/d\phi)_n]_i a}{\Delta\rho_a^T}, \tag{7}$$

where the subscript i refers to the initial damage rates. Using this method, the evaluation of SCP annealing does not depend on the detailed model for normal radiation annealing and requires only that the normal damage rate $(d\Delta\rho/d\phi)_n$ be a linear function of $\Delta\rho$ over the short range of $\Delta\rho$ in which SCP annealing occurs.

EXPERIMENTAL

To measure the electrical resistivity, standard four-probe dc measurements were made. With a 30-mA measuring current, the sensitivity was 2×10^{-11} Ω cm. The range of heavy ions with energies ~ 500 keV in the noble metals is ~ 1000 Å, consequently, it was necessary to use thin-film specimens. Gold, silver, and copper specimens were grown by vapor deposition onto cleavage surfaces of rock salt which were masked in the shape of resistivity specimens. The specimen geometry allowed four segments to be irradiated separately by selectively blocking the ion beam. The pressure in the ion-pumped vacuum chamber during evaporation was $<3\times10^{-7}$ Torr. The films were transferred onto either aluminum or tantalum substrates that had first been oxidized to provide electrical insulation from the films. The specimen thicknesses were determined gravimetrically. The ion beam was produced by a 300-kV accelerator using a Dan-Fysik ion source. Ions with energy >300 keV could be obtained by using multiply charged ions. The ion dose was measured with a Faraday cage that intercepted an annular portion of the ion beam. The beam was swept in the x-y plane during irradiation to ensure a homogeneous beam over the Faraday cage and specimens. The maximum beam power used was 0.2×10^{-7} A at 150 keV, on a 0.1-cm^2 area of the specimen holder (~ 10^{-2} W/cm^2 in the specimen). Measurements of the resistivity with the beam on showed no detectable beam heating of the specimens.

For 500-keV heavy ions, the projectiles were expected to penetrate from 0.2 to 0.6 of the specimen thicknesses.[18] Thus, most of the cascade energy was deposited within the bulk of the specimen, although somewhat inhomogeneously. This damage inhomogeneity can affect the analysis of radiation-annealing experiments in two ways. First, the relationship between the resistivity and the average defect concentration may become nonlinear, and in a thin film the relationship is undoubtably complicated as a result of the electrical size effect. Second, if the ion beam deposits its energy inhomogeneously, then the local concentration of defects in certain regions will be greater than the average concentration in the specimen. However, it is the average defect concentration that is monitored by the resistivity, and consequently, the damage rate for such a case will initially decrease more rapidly with $\Delta\rho$ than if the damage were homogeneous. The same argu-

ment applies to SCP annealing, and therefore, damage inhomogeneities do affect the analysis for the annealing volume V_a. In other work, however, we have found that damage inhomogeneities have little influence on either the initial damage rates or the saturation resistivity if the ions are stopped near the center of the foil.

When using electrical-resistivity measurements to determine the defect concentration in thin films, the size effect in the electrical resistivity usually has to be considered. However, except at low-defect concentrations, the electrical size effect has little effect on damage-rate measurements $d\Delta\rho/d\phi$.[19,20] In the present experiment, the specimens are doped to high-defect concentrations and our analysis makes use of the resistivity behavior only at high-defect concentration. Consequently, no size-effect correction of the data was necessary.

RESULTS

Figures 1(a)–1(c) illustrate the radiation-annealing effects due to energetic cascades described above. These figures show the defect resistivity as a function of proton as well as heavy-ion dose for copper, silver, and gold, respectively. The portions of the curves up to the vertical line show the results for the 150-keV proton irradiations that were carried out near 6 K. In each case, the defect resistivity appears to be approaching a saturation value nearly exponentially. This exponential dose dependence of the resistivity is characteristic of normal saturation effects. At the completion of the proton-doping irradiations, the irradiation particle was switched to self-ions. The effect of these irradiations on the resistivity is shown in the second portions of the curves. In each case, the defect resistivity initially decreases with dose, reaches a minimum, then increases. Finally, the resistivities approach saturation nearly exponentially. For silver, the saturation resistivities for the proton and self-ion irradiations appear almost the same, whereas for copper the saturation resistivity for the proton irradiation is ~25% higher than that for the self-ion irradiation. It has been observed, however, that saturation resistivity values depend somewhat on the range of values of $\Delta\rho$ from which the damage rate curves are extrapolated to zero damage rate and on the procedure for extrapolation.[9] Consequently, the determination of the saturation resistivity here is somewhat ambiguous, especially since size effect corrections have also been omitted in the present work.

To analyze radiation-annealing effects, it is useful to plot the damage rates as a function of

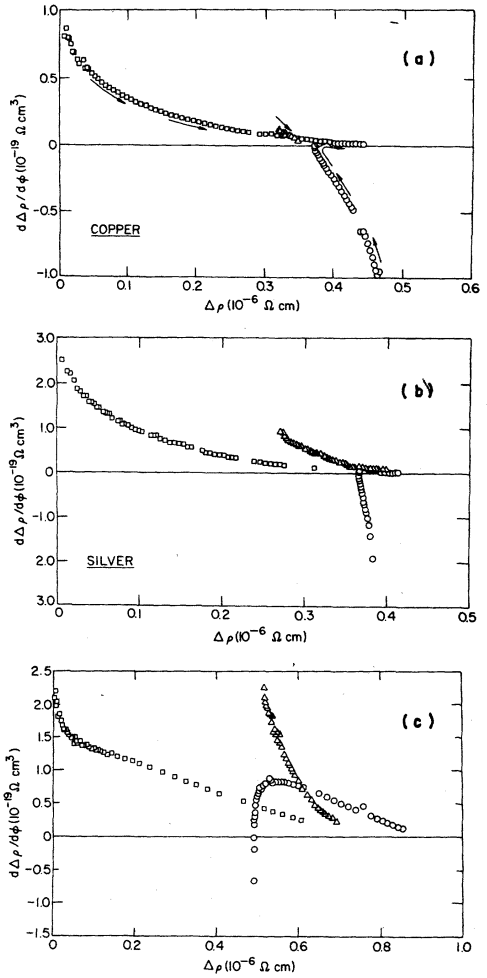

FIG. 2. (a) Representative damages rates for heavy-ion irradiation of copper for, □, undoped specimen; O, specimen doped below 10 K by proton irradiation; Δ, specimen doped above 50 K by proton irradiation. Arrows indicate dose sequence of experiment. (b) Same as (a) for silver. (c) Same as (a) for gold.

$\Delta\rho$. Damage-rate curves for representative heavy-ion irradiations of copper, silver, and gold, are shown in Figs. 2(a)–2(c), respectively, for different doping treatments. The damage rates for the proton-doping irradiations are not of interest here and have been omitted; however, the resistivity increments introduced by these irradiations are given by the starting points of the heavy-ion damage rate curves. Arrows have been included in Fig. 2(a) to show the time (and dose) sequence of the experiment. In each figure, three damage-rate curves appear. One is obtained from an undoped specimen, (no prior proton irradiation, starting at $\Delta\rho = 0$); a second is a specimen doped below 10 K; and a third is for a specimen doped above 50 K. The damage rates for the un-

doped specimens decrease monotonically with $\Delta\rho$ (and dose). This is the normal saturation behavior. The initial curvature in the damage rate is due in part to the size effect in the electrical resistivity (no size-effect correction was made), in part to the inhomogeneity of the damage distribution, and possibly in part to an intrinsic nonlinearity of the damage rate with dose.[10,21] Linear extrapolation of these curves to zero damage rate yielded the saturation resistivities given above.

The damage rates for the specimens doped below 10 K are influenced by both normal radiation and SCP annealing effects. The SCP annealing dominates the initial damage rates, causing them to be negative for sufficiently high doping treatments. As the heavy-ion irradiation is continued, the SCP effect saturates, and the damage rate goes through a maximum, which is always positive. Finally, the damage rate decreases and approaches the normal radiation-annealing behavior. It can be seen from Figs. 1 and 2 that the SCP annealing saturates at a much lower dose than the defect production. Also, after the SCP annealing does saturate, the damage-rate curves become nearly linear. These features are in agreement with the radiation-annealing model used here.

The damage rates for the specimens doped above 50 K are similar to those with no doping. The damage rates are initially positive and decrease monotonically with dose. The initial damage rates are, however, higher than the undoped damage rates at a particular $\Delta\rho$, see Figs. 2(a)–2(c). This is in contrast to what is expected on the basis of the simple saturation model given by Eq. (3). This is not too surprising since the model, as pointed out above, assumes that the ratio of the spontaneous recombination volume-to-resistivity per defect is independent of the way in which the defect is produced. For the 50-K proton-doping irradiations, interstitials are able to migrate and form clusters, and clustering is expected to reduce the average recombination volume. Clustering, however, also occurs in energetic displacement cascades as a result of the high spatial correlations between defects.[7] If the enhanced damage rates after the 50-K doping irradiations were entirely due to clustering effects, these results would indicate that defects produced by a proton irradiation at 50 K are more clustered than defects produced in cascades below 6 K. This issue is complicated in the present experiment, however, by the fact that the damage produced by the heavy-ion irradiation is distributed inhomogeneously in the specimen. As noted above, the saturation effects appear stronger for a given value of $\Delta\rho$ if the damage is produced inhomogeneously. The defects produced by the 50-K proton irradiation are distributed homogeneously, whereas those produced by heavy ions stopped within the specimen are not. Consequently, the heavy-ion irradiation will have a higher damage rate if the specimen has been irradiated to a given $\Delta\rho$ by 50-K proton irradiation than if it has been irradiated to the same $\Delta\rho$ by an inhomogeneous heavy-ion irradiation (undoped). The results in fact show that the effect is greatest in gold and silver and very small in copper, and it is for the gold and silver that inhomogeneity is expected to be more serious. However, neither argument, inhomogeneity nor clustering, seems entirely capable of explaining the very high damage rate in gold after the 50-K proton irradiation.

With regard to the analysis of SCP annealing, the effect of clustering and inhomogeneity in the damage should not be very important for two reasons. First, the interstitials produced during the doping irradiation are not mobile, therefore little defect clustering should occur during doping. Second, the normal radiation-annealing parameters in Eq. (5) are extracted from the data observed immediately after SCP annealing saturates and not from a different specimen. This minimizes the effects of damage inhomogeneities or effects of clustering in the cascades. Therefore, unless the normal damage rate is very nonlinear in $\Delta\rho$ over the region in which SCP annealing occurs, the analysis should be reasonably accurate. For the case of doping to high-defect concentrations, cascade defect clustering is insignificant regarding the SCP analysis since initially the number of defects produced is much smaller than the number annihilated by SCP events. Consequently, an error in determining the number of cascade defects which are produced and must be subtracted from the measured damage rates to obtain the SCP annealing, is not serious. Moreover, the annealing volumes in silver obtained for the cases in which (i) a large number of defects are produced in contrast to those annihilating (low doping concentration), and (ii) few defects are produced in contrast to those annihilating (high doping concentration) differ by less than a factor of 2, 6.2×10^{-16} cm^3 compared with 3.9×10^{-16} cm^3; this is also true for copper. This difference may result from inadequacies in the model because of either clustering or damage inhomogeneities, although the specimen thicknesses were the same for these cases. On the other hand, it cannot be excluded that the observed differences in the annealing volumes indicate a slight concentration dependence of V_A. In any case, the differences are relatively small and it would therefore seem that the linear

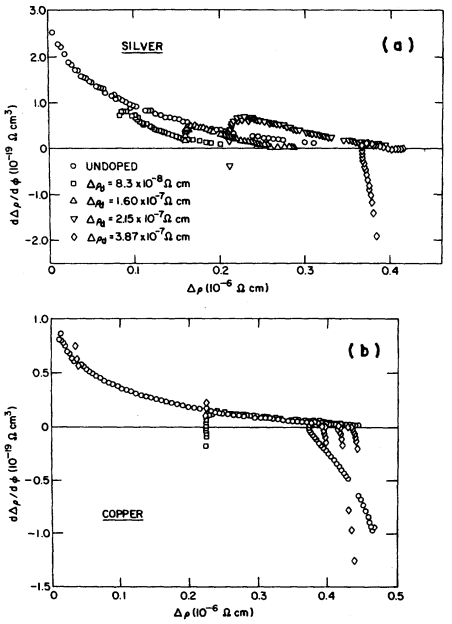

FIG. 3. (a) Effect of doping concentration by 150-keV proton irradiation on self-ion damage rates for silver. Specimen thicknesses in nm are ○, 239; □, 348; △, 348; ▽, 239; and ◇, 348. (b) Effect of doping concentration by 150-keV proton irradiation on argon damage rates in copper, open symbols; the ◇ indicate 400-keV bismuth damage rates intermixed with argon damage rates. Specimen thicknesses are 310 nm.

annealing model is adequate.

The values for $\Delta\rho_a^T$ and V_a are obtained from the data in Figs. 2(c) and 3(a) and 3(b). This was done as outlined above; N_F^c and V_r are first obtained from the high-dose data by extrapolating $d\Delta\rho/d\phi$ to both zero $\Delta\rho$ and zero damage rate. $(d\Delta\rho/d\phi)_s$ is then plotted versus $\Delta\rho_a$ by integrating Eq. (6) to obtain $\Delta\rho_a$. Representative plots are shown for the three metals in Figs. 4(a)–4(c). Extrapolating $(d\Delta\rho/d\phi)_s$ to zero yields $\rho_F C_P$. V_a is then determined from Eq. (7). The results are given in Table I.

The effect of the Frenkel-pair concentration on SCP annealing was examined by varying the dose of the doping irradiation in several copper and silver specimens. The damage rates for these specimens are shown in Figs. 3(a) and 3(b), and the results for the annealing volumes and total recovery are in Table I. [To quantitatively compare damage rates from different specimens, it is necessary to normalize the data by multiplying $d\Delta\rho/d\phi$ by the specimen thickness, cf. Eq. (5).] It can be seen in the table that, in both copper and silver, the fractional SCP recovery $\Delta\rho_a^T/\Delta\rho_d$, where $\Delta\rho_d$ is the doped-in resistivity increment, increases rapidly with $\Delta\rho_d$, particularly in copper.

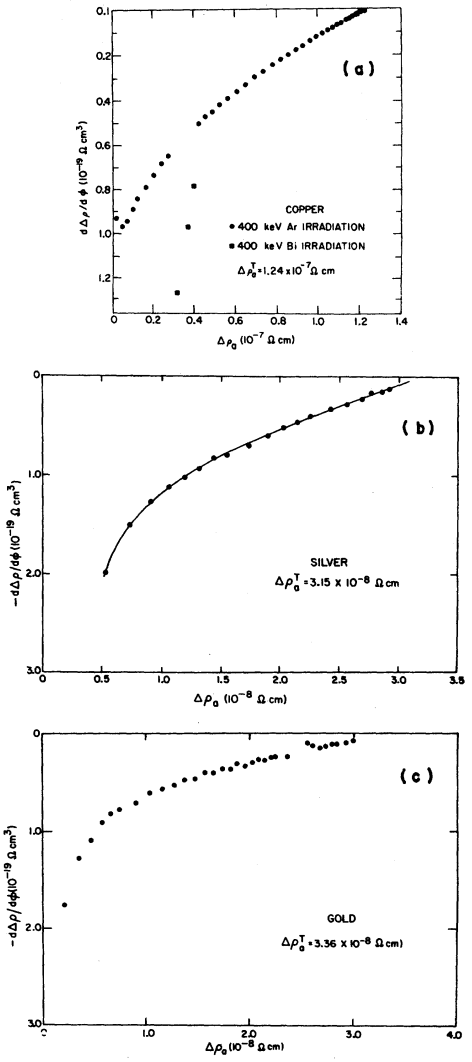

FIG. 4. (a) Representative damage rates for SCP annealing vs recovery for copper. (b) Same as (a) for silver. (c) Same as (a) for gold.

The annealing model however, assumes that $\Delta\rho_a^T$ is a linear function of close-pair concentration. One explanation for the fact that C_P increases faster than linearly with $\Delta\rho_d$ is that, as the defect concentration becomes large, an interstitial not close to its own vacancy or one which initially jumps away from its own vacancy, has a finite probability to recombine with another vacancy by SCP events. These recombinations are much less probable at low-defect concentration due to the limited number of jumps that the interstitial can make in the duration of the cascade event.

Table I shows that the annealing volumes V_a are nearly constant for a given metal, projectile mass, and cascade energy. The weak dependence on $\Delta\rho_d$ is in agreement with the assumption that

TABLE I. Results for the SCP annealing volumes and total SCP annealing for several targets, projectiles, and doping concentrations. Here a is the specimen thickness, E is the projectile energy, E_D is the damage energy, $\Delta\rho_d$ is the doped-in defect concentration, $\Delta\rho_d^T$ is the total resistivity annealed by SCP events $(d\Delta\rho/d\phi)_s$ is the initial SCP annealing rate, and V_a is the SCP annealing volume for each cascade.

Specimen	a (cm)	Projectile	E (keV)	E_D (keV)	$\Delta\rho_d$ (Ω cm)	$\Delta\rho_d^T/\Delta\rho_d$	$\left(\frac{d\Delta\rho}{d\phi}\right)_s a$ (Ω cm^4)	V_a (cm^3)
Ag	3.48×10^{-5}	Ag	500	299	8.3×10^{-8}	0.02	1.05×10^{-24}	6.2×10^{-16}
Ag	3.48×10^{-5}	Ag	500	299	1.60×10^{-7}	0.02	1.98×10^{-24}	6.0×10^{-16}
Ag	2.39×10^{-5}	Ag	500	299	2.14×10^{-7}	0.05	5.10×10^{-24}	5.1×10^{-16}
Ag	3.48×10^{-5}	Ag	500	299	3.87×10^{-7}	0.07	1.09×10^{-23}	3.9×10^{-16}
Au	2.35×10^{-5}	Au	540	244	4.94×10^{-7}	0.05	5.5×10^{-24}	2.1×10^{-16}
Cu	3.10×10^{-5}	Ar	400	162	2.23×10^{-7}	0.04	3.65×10^{-25}	4.4×10^{-17}
Cu	3.10×10^{-5}	Ar	400	162	4.70×10^{-7}	0.26	3.35×10^{-24}	2.7×10^{-17}
Cu	3.10×10^{-5}	Cu	400	222	4.46×10^{-7}	0.22	4.02×10^{-24}	4.1×10^{-17}
Cu	2.20×10^{-5}	Au	870	508	4.10×10^{-7}	0.16	1.02×10^{-23}	1.6×10^{-16}

a cascade will cause agitation of the lattice sufficient to cause recombinations of close pairs within a certain well-defined volume. It is quite remarkable however, that a 500-keV silver self-ion cascade gives an annealing volume which is more than a factor of 10 larger than a 400-keV Cu or Ar cascade in copper, although according to the random theory, the cascade volume is expected to be somewhat larger for the copper cascades.[22] As will be discussed below, this effect is connected with the details of the energy deposition in very energetic cascades. To observe the effects of the cascade-energy density on the SCP annealing, 400-keV Bi^{++} test irradiations were intermixed with the 400-keV Ar^{++} irradiation of copper. The higher mass projectile produces cascades of greater energy density. The damage rates for the 400-keV Bi irradiation are indicated by ◇ in Fig. 3(b), and it is observed that SCP annealing is initially greater for the Bi irradiation. The enhancement may be due to the fact that electronic losses are lower for the Bi irradiation than for the Ar. The effect of this higher-damage energy, ~25% higher for the Bi irradiation, is seen by an enhancement of the damage rate of ~25% in the undoped specimen. The additional SCP annealing for the Bi irradiation, however, is considerably larger than the difference in damage energies. Qualitatively this is clearly seen in Fig. 3, although the Ar irradiation prior to the Bi irradiation makes the analysis complicated and also precludes determining the annealing volume for the Bi irradiation. Three Bi irradiations were also carried out at the completion of the Ar irradiations. These curves start with negative damage rates at a damage state which showed positive damage rates for the Ar irradiation, and clearly indicate that the SCP annealing effect is stronger for Bi cascades. The fact that some stage I interstitials can be annealed by superposition of Bi cascades onto Ar cascades in Cu is consistent with isochronal annealing data[16] which show that stage I recovery of the electrical resistivity for Ar cascades in Cu at similar defect concentrations as used here, is 10%, whereas stage I recovery for Bi cascades in Cu is <5%.

To further examine the effect of energy density in the cascade on SCP annealing, 870-keV gold ions were used to irradiate doped-copper specimens. For this case, the annealing volume is increased almost a factor of 6 compared with that for the Ar irradiation at similar values of $\Delta\rho_d$ (although $\Delta\rho_d$ is slightly greater for the Ar irradiation, it was noted above that V_a does not vary greatly with the doped-in defect concentration). The initial SCP annealing rate is a factor of 3.6 and 4.3 greater for the 870-keV gold irradiation than for the 400-keV self-ion or Ar irradiation, respectively. It the specimen thicknesses are taken into account, however, and the number of recombinations per incident ion/cm^2 is considered rather than $(d\Delta\rho/d\phi)_s$, the SCP annealing ratios given above are reduced to 2.6 and 3.1, respectively. The latter ratios are almost exactly the same as the ratios for the damage energies for the different irradiations. Presumably, the ratios for the initial SCP annealing would increase somewhat if the values of $\Delta\rho_d$ were exactly the same (see Table I), since as mentioned above the SCP annealing varies strongly with $\Delta\rho_d$.

In summary, the results show that SCP annealing occurs in copper, silver, and gold for specimens doped by 150-keV proton irradiations at temperatures below 10 K but does not occur if the doping irradiations are carried out near 50 K. It was observed that the effectiveness of

SCP annealing, as evaluated by the ratio $\Delta\rho_d^T/\Delta\rho_d$, increases with doped in defect concentration $\Delta\rho_d$. Finally, the volumes around the cascade in which SCP annealing occurs were obtained. It was found that the annealing volumes are largest for the energetically densest cascades.

DISCUSSION

The main result of the present work is contained in the observation that close Frenkel-pair configurations are unstable in the vicinity of energetic displacement cascades. This cascade annealing effect may be a principal reason for the low-defect production in cascades at low temperature. Binary-collision calculations[23,24] and analytical models[25] predict that the number of defects produced in cascades should be close to the modified Kinchin-Pease result, $N = 0.8E_D/2E_d$, where E_d is the average threshold energy. Experimentally it is found that for low-energy recoils, this rule is obeyed,[26] whereas for high-energy recoils, defect production is ~0.35 times the theoretical value.[27] The transition from high-to-low defect-production efficiency occurs in Ag near 2 keV.[26] When calculating defect production, the binary-collision calculations of Robinson and Torrens determine the stability of Frenkel pairs by two methods.[23] In one, the "threshold model" the threshold energy is chosen to take into account the stability of Frenkel pairs. A somewhat more satisfactory procedure is given by the "capture model" in which the stability of the Frenkel pair is determined by the spontaneous recombination volume around each vacancy in which an interstitial is unstable. This model has the advantage that recombinations of interstitials with vacancies other than their own are taken into account, a situation that is probable in very dense cascades. Neither model includes the stimulated recombination of close pairs. In contrast to the binary collision calculations, Guinan[11] has calculated defect production in cascades using a fully dynamical computer simulation similar to the type developed at Brookhaven.[28] For a 2.5-keV cascade in tungsten, he has found that after the displacements have ended, the agitation in the lattice causes many Frenkel pairs to recombine that otherwise would be stable. Vineyard has considered thermal-spike phenomena on the basis of the classical heat equation.[29] For a spherical δ-function spike, it was found that the number of jumps made by the migrating defect depends on the damage energy to the $\frac{5}{3}$ power. Although no detailed comparison is made between the results of the present experiment and this theory, it is observed that the SCP annealing does increase with damage energy and probably somewhat faster than linearly as indicated by the initial SCP annealing for Au, Bi, Cu, and Ar irradiation of Cu. In the present investigation, cascade energies near 500 keV were used. For a description of such energetic cascades, the assumption of a spherical spike is clearly not adequate. It has been shown that at those energies cascades in Au and Ag exhibit a pronounced subcascade structure.[30,31] It has also been pointed out that subcascade formation is a general feature of energetic cascades[32] and indications exist[31] that Cu shows a much more pronounced splitting into subcascades than either Ag or Au. If the observed SCP annealing takes place within a region around each subcascade, the fact that the SCP annealing volume in copper is about a factor of 10 smaller than in Au and Ag can be understood. Each subcascade in Cu would then be associated with a much smaller damage energy than, for example, a subcascade in Ag. Since, as the results of Vineyard indicate, the volume around a spherical spike in which SCP annealing takes place increases with energy much more strongly than linearly, one can easily see that the total SCP annealing volume in a cascade can be drastically reduced when at a given damage energy the number of subcascades is increased. Comparison of the SCP annealing volumes in Ag and Au with transmission-electron microscopy observations of subcascade formation shows that the SCP annealing volumes around each subcascade overlap. Therefore, the total cascade structure can be viewed as being embedded in the SCP annealing volume. In contrast to this, a comparison of the Cu SCP annealing volume with the damage volume, as indicated for example by the dimensions connected with the energy deposition in the random-cascade theory,[22] shows that the SCP annealing volume in a 500-keV cascade in copper most probably is not completely connected. Although the present work has shown the basic phenomenon of SCP annealing within the cascade region, it should be pointed out that the magnitude of the annealing of predoped Frenkel pairs, falls considerably short of that necessary to account for the low-defect production efficiencies in cascades. However, this is not unexpected since the detailed production process of defects produced in a cascade is almost certainly different from that for a cascade superimposed onto a preexisting population of defects introduced by a proton irradiation.

The results of the present paper also have a direct bearing on the question of the saturation concentrations of defects obtained by different particle irradiations. In copper the saturation resistivities are 0.76 and 0.62 $\mu\Omega$ cm for elec-

tron[8] and 150-keV proton irradiations, respectively, whereas for fission fragment and heavy-ion irradiations, the value is 0.48 $\mu\Omega$ cm.[9] If one considers only the concept of a spontaneous recombination volume without allowing for SCP annealing, these differences in the saturation resistivities are difficult to understand. This is because in cascades the high density of defects, and the segregation of interstitial and vacancies, should lead to overlapping of recombination volumes. The average recombination volume would therefore be reduced and the saturation resistivity increased.[4-7] SCP annealing on the other hand increases the effective recombination volume in a cascade, so that the saturation resistivity may decrease, as is observed in copper and platinum. In silver the saturation resistivities are ~0.50 $\mu\Omega$ cm for various types of particle irradiation.[9] This occurs presumably because both mechanisms described above are operative; the effective recombination volume (i) is increased due to SCP annealing and (ii) is decreased because of defect clustering in the cascade. Since the saturation resistivities are about the same, the effect of the two mechanisms must essentially cancel.

The effect of SCP annealing on stage I recovery is straightforward. Close-pair recombinations comprise a significant fraction of stage I recovery and hence elimination of close pairs during the cascade event should reduce the recovery observed by thermal annealing. It has in fact been shown that stage I isochronal recovery is greatly reduced as the energy density in the cascade is increased.[16] Previously, the small fraction of recovery in stage I after fast-neutron irradiation has been explained on the basis of a segregation of vacancies and interstitials. The segregation results from the ejection of interstitials out of the center of cascade region and the preferential survival of clusters of vacancies and interstitials due to mutual trapping processes.[33] The present experiment suggests that another mechanism, SCP annealing within the cascade, may be important in accounting for the reduced stage I recovery in cascades as this mechanism removes close pairs and possibly enhances interstitial clustering during the cascade event. Moreover, it has been shown that stage I recovery after fast neutron irradiation is 15% for Ag and 31% for Cu.[17] Stage I recovery is also greater in Cu than in Ag for heavy-ion irradiations.[16] These isochronal recovery results appear consistent with the conclusion obtained here that in Ag the entire subcascade structure is embedded in the SCP annealing volume but not in copper. The unannealed region in the copper cascades are thus able to contribute to stage I annealing.

Finally, it is noted that the SCP annealing effect in gold is similar to that in copper and silver. Radiation annealing in gold has also been observed during subthreshold electron irradiations, and was reported to disappear when the specimen was annealed to 22 K. This has been interpreted as evidence for a close-pair configuration that is stable in Au up to ~22 K.[34] The present observations support such a view. Stage I in copper and silver is well understood, and it is known that interstitials are immobile below 10 K. In gold however, interstitial clustering has been observed at 5 K, indicating long-range transport of interstitials below that temperature.[35] Therefore, the possibility exists that free migration of interstitials may take place at our lowest irradiation temperature in Au. Although a close pair with an activation energy higher than that for free migration of interstitials has not been observed in other fcc metals, such evidence does exist for tungsten and molybdenum.[36,37] The question regarding free migration below 4 K in Au cannot be answered from the present observation, however the existence of a close-pair configuration is consistent with the present results.

ACKNOWLEDGMENTS

The authors are grateful for helpful discussions with R. Benedek, T. H. Blewitt, R. C. Birtcher, and F. A. Nichols. The help of W. E. King given in the initial phase of the experiments and the continued technical assistance by L. J. Thompson, L. R. Singer, and J. R. Wrobel are gratefully acknowledged.

---

*Work supported by the U. S. ERDA.

[1](a) See, e.g., Fundamental Aspects of Radiation Damage in Metals, edited by M. T. Robinson and F. W. Young, U.S. ERDA CONF-751006-P1, Vol. 1, 1975 (unpublished); or (b) *Vacancies and Interstitials in Metals*, edited by A. Seeger, D. Schumacher, W. Schilling, and J. Diehl (North-Holland, Amsterdam, 1970).

[2]P. Lucasson, in Ref. 1a, p. 42.

[3]M. T. Robinson, in Ref. 1a, p. 1.

[4]K. Dettmann, Phys. Status Solidi 10, 269 (1965).

[5]K. Dettmann, G. Leibfried, and K. Schroeder, Phys. Status Solidi 22, 423 (1967).

[6]G. Lück and R. Sizmann, Phys. Status Solidi 5, 683 (1964).

[7]H. J. Wollenberger, in Ref. 1b, p. 215.

[8]G. Duesing, H. Hemmerich, W. Sassin, and W. Schilling, Proceedings of the International Conference on Vacancies and Interstitials, Jülich, Germany, Vol. I,

246, 1968 (unpublished).
[9]R. C. Birtcher and R. S. Averback (unpublished).
[10]W. Kesternich and K. L. Merkle, in *Application of Ion Beams to Metals*, edited by S. T. Picraux, E. P. EerNisse, and F. L. Vook (Plenum, New York, 1974), p. 495.
[11]M. Guinan (private communication).
[12]R. S. Averback and K. L. Merkle, in Ref. 1a, U.S. ERDA CONF-751006-P2, 1976, Vol. 2 (unpublished), p. 1048.
[13]J. A. Brinkman and W. S. Gilbert, U. S. Atomic Energy Commission Report No. NAA-SR-262 (1953) (unpublished).
[14]D. Schmidt, Ph.D. thesis (Lawrence Radiation Lab., Univ. of Calif., UCRL-51009, 1971) (unpublished).
[15]R. S. Averback (unpublished).
[16]R. S. Averback, L. J. Thompson, and K. L. Merkle, International Conference on Atomic Defects in Metals, Argonne, Ill., 1976 (unpublished).
[17]J. A. Horak and T. H. Blewitt, J. Nucl. Mater. 49, 161 (1973).
[18]H. E. Schiøtt, Radiat. Eff. 6, 107 (1970).
[19]F. Dworschak, H. Schuster, H. Wollenberger, and J. Wurm, Phys. Status Solidi 21, 741 (1967).
[20]K. L. Merkle and L. R. Singer, Appl. Phys. Lett. 11, 35 (1967).
[21]G. Burger, H. Meissner, and W. Schilling, Phys. Status Solidi 4, 28 (1964).
[22]K. B. Winterbon, P. Sigmund, and J. B. Sander, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. 37, 14 (1970).
[23]M. T. Robinson and I. M. Torrens, Phys. Rev. B 9, 5008 (1974).
[24]T. R. Beeler, Phys. Rev. 150, 470 (1966).
[25]P. Sigmund, Radiat. Eff. 1, 15 (1969).
[26]K. L. Merkle, R. S. Averback, and R. Benedek, Phys. Rev. Lett. 38, 424 (1977).
[27]R. S. Averback, R. Benedek, and K. L. Merkle, in Ref. 16.
[28]J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. 120, 1229 (1960).
[29]G. H. Vineyard, Radiat. Eff. 29, 245 (1976).
[30]K. L. Merkle and R. S. Averback, in Ref. 1a, p. 127.
[31]K. L. Merkle, Phys. Status Solidi 18, 173 (1966).
[32]K. L. Merkle, in *Radiation Damage in Metals*, edited by N. L. Peterson and S. D. Harkness (American Society for Metals, Metals Park, Ohio, 1976), p. 58.
[33]W. Schilling, G. Burger, K. Isebeck, and H. Wenzl, in Ref. 1b, p. 288.
[34]H. E. Shepp, F. Dworschak, and H. Wollenberger, Radiat. Eff. 7, 219 (1971).
[35]P. Ehrhart and E. Segura, in Ref. 1a, CONF-751006-P2, Vol. 2, p. 295.
[36]F. Dausinger and H. Schultz, in Ref. 1a, CONF-751006-P2, Vol. 2, p. 438.
[37]S. Okuda, *Proceedings of the International Conference on Defects and Defect Clusters in B.C.C. Metals and Their Alloys*, edited by R. J. Arsenault (Natl. Bur. Stds., Gaithersburg, Md., 1973), Vol. 18, p. 51.