PHYSICAL REVIEW VOLUME 140, NUMBER 3A 1 NOVEMBER 1965

Stage III Annealing in Proton-Irradiated Noble Metals*

F. Dworschak† and J. Koehler

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

(Received 15 June 1965)

Pulsing and annealing data are given for 99.999% pure copper specimens which have been proton irradiated at 90°K. It is shown that stage II obeys first-order annealing kinetics and that the structure observed is probably not associated with impurities. Stage III obeys second-order kinetics, and its activation energy in the case of copper is not dependent on dose in the range $\Delta\rho_0=3\times10^{-9}\ \Omega$ cm to $\Delta\rho_0=3\times10^{-8}\ \Omega$ cm. Pulsing experiments in which samples are heated in a msec from -50°C to temperatures up to 230°C and held for 30 msec before quenching show no evidence for any change in the annealing process (i.e., the results can be predicted assuming $E_M{}^{\mathrm{III}}$ (Cu)$=0.71$ eV and using second-order kinetics). It is shown that if di-interstitial migration is responsible for stage III then the binding energy of di-interstitials exceeds 1.0 eV in copper. If, conversely, two kinds of interstitials migrate in stages I and III, then the pulsing experiment suggests that the barrier preventing conversion of the stage III type to the stage I type is greater than 1.14 eV in copper. No evidence for vacancy migration in proton-irradiated silver is observed during annealing at temperatures above stage III. Existing models suggested to explain the annealing of irradiation damage are reviewed.

I. INTRODUCTION

In a previous paper[1] a number of experiments on stage III annealing of proton-irradiated noble metals have been reported. On the basis of the results a definite answer as to which physical process is responsible for stage III annealing could not be given. In the case of copper and silver two of the proposed models could both equally well describe stage III annealing and as yet there is no direct evidence against either mechanism. One of the models (A) explains stage III annealing by the migration of interstitial clusters (di-interstitials), whereas the other (B) assumes the existence of two kinds of interstitials, one migrating in stage I and the other migrating in stage III.

The present experiments were carried out to furnish direct evidence which we hoped would distinguish between the models and to investigate stage II and III annealing in copper more closely. The specimens were irradiated at liquid-nitrogen temperatures with 10-MeV protons and were then subjected to a number of different annealing procedures during which the changes in the electrical resistivity were measured.

II. EXPERIMENTAL PROCEDURE

The specimens were 5-mil diam wires prepared from 99.999+% pure copper obtained from the ASARCO in the form of a $\frac{3}{8}$-in. rod. The specimen preparation and mounting on the blocks, as well as the irradiation and the annealing procedures have been described in a previous paper.[1] The residual resistivity of the mounted copper specimens was between 1.72×10^{-9} and 1.54×10^{-9} Ω cm.

Nine specimen holders, each containing two specimens, were irradiated at liquid-nitrogen temperatures, each holder in a different irradiation run. After the irradiation of a specimen holder it was transferred from the liquid-nitrogen irradiation jig into a liquid-nitrogen storage Dewar. The dose dependence of the recovery stages was investigated by varying the integrated flux of the different runs.

III. PULSING

If stage III annealing in copper involves the migration of an interstitial cluster, it should be possible to break up this complex by pulsing the irradiated sample to a given temperature for short periods. By pulsing, it shall be understood that the temperature of a specimen follows a square wave. In this recovery model, it is assumed that single interstitials migrate in stage I, i.e., their energy of migration is 0.1 eV. The annealing during an ideal pulse can then be described by the following rate equations:

Reactions involving I_2: Reactions involving I:

$$\begin{array}{ll} I_2+V\rightarrow I\,, & I+I\rightleftarrows I_2\,,\\ I_2\leftrightarrows I+I\,, & I+V\rightarrow \text{ann.},\\ I_2+I\rightarrow I_3\,. & I+I_2\rightarrow I_3\,. \end{array}$$

Reactions involving V: Reactions involving I_3:

$$\begin{array}{ll} V+I\rightarrow \text{ann.}, & I_3\leftarrow I+I_2\,.\\ V+I_2\rightarrow I\,. & \end{array}$$

I_2, V, I, and I_3 are the concentrations (atomic fractions) of di-interstitials, vacancies, interstitials, and tri-interstitials. It has further been assumed that during the pulse vacancies and tri-interstitials are immobile and do not break up, and that divacancies are not present. The differential equations for these reactions can

---

* Supported in part by the U. S. Atomic Energy Commission under Contract No. AEC-1198-K.

† Present address: Institute fur Reaktorwerkstoff, Technische Hochschule von Aachen, Aachen, Germany.

[1] F. Dworschak, K. Herschbach, and J. S. Koehler, Phys. Rev. 133, A293 (1964).

be written as

$$\frac{dI_2}{dt}=-K_1e^{-E_m{}^2/kT}I_2V-K_2e^{-(E_m{}^I+B^2)/kT}I_2 +K_3e^{-E_m{}^I/kT}I^2-K_4e^{-E_m{}^I/kT}II_2, \quad (1)$$

$$\frac{dI}{dt}=+K_1e^{-E_m{}^2/kT}I_2V+2K_2e^{-(E_m{}^I+B^2)/kT}I_2 -2K_3e^{-E_m{}^I/kT}I^2-K_4e^{-E_m{}^I/kT}II_2-K_5e^{-E_m{}^I/kT}IV, \quad (2)$$

$$\frac{dV}{dt}=-K_1e^{-E_m{}^2/kT}I_2V-K_5e^{-E_m{}^I/kT}IV, \quad (3)$$

$$\frac{dI_3}{dt}=K_4e^{-E_m{}^I/kT}II_2, \quad (4)$$

where $E_m{}^2$ and $E_m{}^I$ are the migration energies of di-interstitials and interstitials and B^2 is the binding energy of a di-interstitial. k is the Boltzmann constant and K_1, K_2, K_3, K_4, and K_5 are constants consisting of the frequency factor, a combinatory number and the entropy factor. These differential equations could not be solved analytically and therefore they were solved numerically using a computer.

After each pulse the temperature of the pulse was raised by 30°C. The solutions that are given in Fig. 1 show the influence of the value B^2 on the defect concentrations after pulsing to successively higher temperature for 0.03 seconds. The solutions have been calculated for the following constants and initial concentrations. $K_1=7.10^{13}$, $K_2=K_1$, $K_3=K_1$, $K_4=K_1$, $K_5=K_1$, and $E_m{}^2=0.7$ eV. $I_2=1\times10^{-5}$, $V=2\times10^{-5}$, $I=I_3=0$.

The change of the resistivity that is connected with these defect concentrations has then been calculated on the assumption that $\Delta\rho={}_{1\%\text{ vacancies}}=1.5\Delta\rho_{1\%\text{ interstitials}}=\frac{1}{2}\Delta\rho_{1\%\text{ di-interstitials}}=\frac{1}{3}\Delta\rho_{1\%\text{ tri-interstitials}}$. The results are shown in Fig. 2 ($\Delta_{\rho\ 1\%\text{ vacancies}}=1.5\times10^{-6}\Omega$ cm).

There are two annealing processes which can give rise to a decrease in resistivity during a pulse. First, even if no breakup of a complex occurs, there will be some annealing because the complex moves with migration energy $E_M{}^2$. Since stage III annealing is of second-order we attempt to keep the amount of annealing by complex motion low by using low concentrations and by keeping the pulse short. Second, if the complex breaks up into parts one of which moves with a low-migration energy, then as the curves in Fig. 2 demonstrate a rapid annealing will occur at a pulse temperature which is determined by the binding energy of the complex. If the binding energy is very large (under the conditions described here if B_2 exceeds 1.0 eV) then the annealing associated with stage III annealing is appreciable during the pulse so that it becomes impossible to determine whether defect breakup has occurred. Since the damage concentration must be kept larger than the impurity concentrations, we can only work at damage concentrations of about 10^{-5}. In addition, if we wish to use a well-defined pulse, the total pulse time should be considerably longer than the rise time which is about 10^{-3} sec in these experiments. As a result, we were only able to detect breakup for binding energies equal to or less than 1.0 eV.

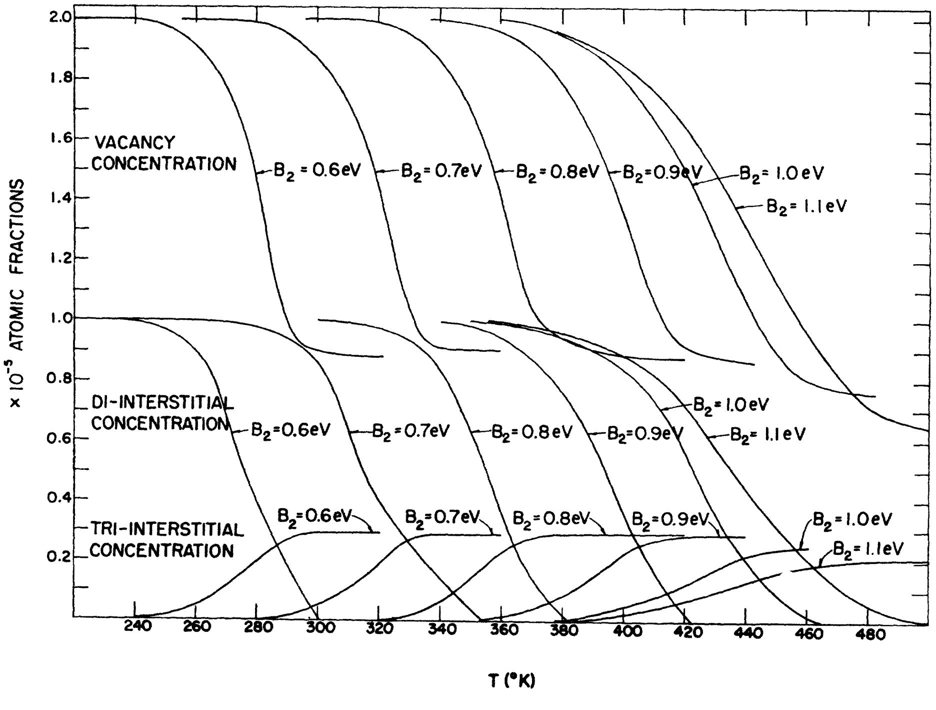

FIG. 1. Calculated atomic fractions of vacancies, di-interstitials, and tri-interstitials after pulsing from 223°K to the temperatures shown. Initially $I_2=1\times10^{-5}$, $V=2\times10^{-5}$. B_2 is the di-interstitial binding energy. $B_3=\infty$. Pulse time is 3×10^{-2} sec.

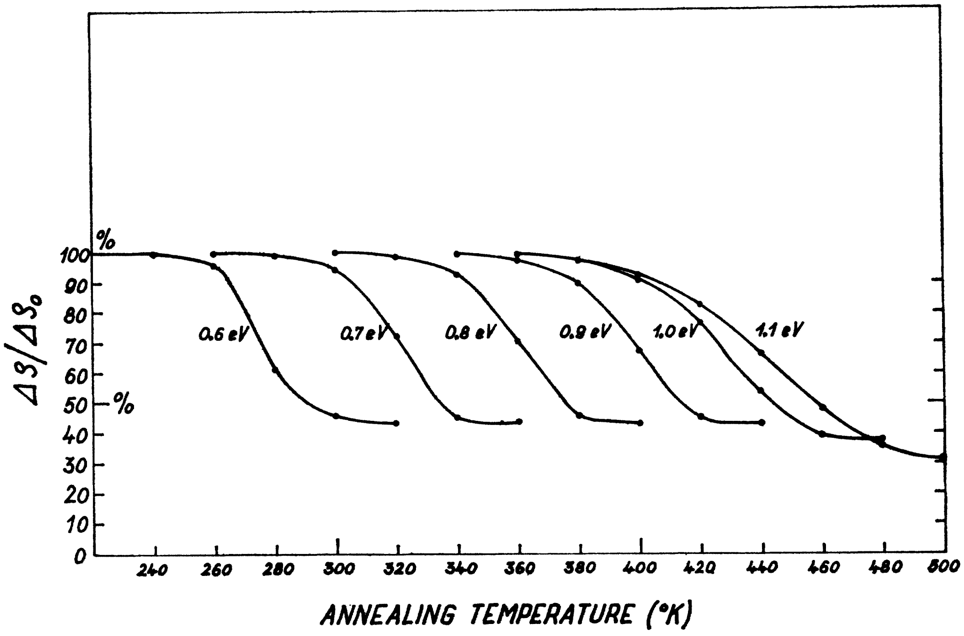

FIG. 2. Calculated decreases in resistivity after pulsing from 223°K to the temperatures shown.

IV. PULSING EXPERIMENTS

The irradiated specimens that were to be pulsed were annealed at $-50°C$ for 64 min in order to anneal out the defects migrating before stage III. The specimens were then kept in their specimen holder in a temperature bath of $-50°C$, while a shaped dc current was sent through them. In a time of about 0.001 sec the specimens could be heated to a predetermined temperature and could be held at this temperature for 0.03 seconds. After this time, the current was switched off and the specimens were cooled by conduction through the sample and the helium exchange gas to the temperature of the aluminum block which was $-50°C$.

The circuit used for pulsing is described in the Appendix. The temperature reached during the pulse is obtained by measuring the resistance of the portion of the sample between the potential leads. The voltage drop across the gauge length is followed by photographing the cathode-ray tube trace obtained during a pulse. The constant current flowing through the specimen during all except the initial heating portion of the pulse is measured by running the specimen current through a resistor which is matched in resistance to the specimen and its current leads at 0°C. Since the resistance of the specimen increased during the largest pulses from about 0.01 to 0.028 Ω, and since the resistance of specimen plus leads was about 0.33 Ω, the constant current measured was too high by about 6% in the case of the largest pulses. A correction to the current proportional to the voltage across the specimen has been made to eliminate this error. The voltage across the specimen is in most cases constant to $\pm\frac{1}{2}\%$ during the pulse. This implies that the specimen temperature is constant to $\pm 2°C$ during the largest pulses and $\pm 1°C$ during pulses below 100°C. The resistance of the specimen prior to irradiation is known at 0°C. From the current and voltage during the pulse, its resistance at the pulse temperature is known. Using the known variation of the resistivity of copper versus temperature, the specimen temperature is calculated. Note that the resistance changes introduced by irradiation were in all cases less than 0.45% and in the low-dose pulse experiments were about 0.12%.

In trial runs 0.6-mil diam wires were spotwelded at different positions to the specimen so that the potential drop across various portions of the specimen could be recorded separately during a pulse. One found that the temperature is a maximum at the center of the specimen and deviates by less than $\pm 5°C$ from the measured pulse temperature over the gauge length used. In summary, we believe that the pulse temperature is constant and is measured to within $\pm 5°C$ for pulses to 200°C and above. The pulse temperature is constant and is known to $\pm 3°C$ for pulses to 100°C.

The samples were pulse-heated for 0.03 sec to successively higher temperatures. After each pulse the specimens were cooled to 4.2°K and the residual electrical resistance was determined. In Fig. 3 the results are shown for samples that had been irradiated with a total dose of 1.1×10^{16} p/cm^2. The data show the percentage of the resistivity increase that was left after each pulse.

The residual resistivity decreases gradually with increasing pulse temperatures and shows no evidence for a breakup process.

In order to compare the pulse data with those of an isothermal annealing run at a temperature where no breakup occurs, the time for each pulse was normalized to a time for a constant annealing temperature by the following equation

$$te^{-E_M/kT}=t'e^{-E_M/kT'},$$

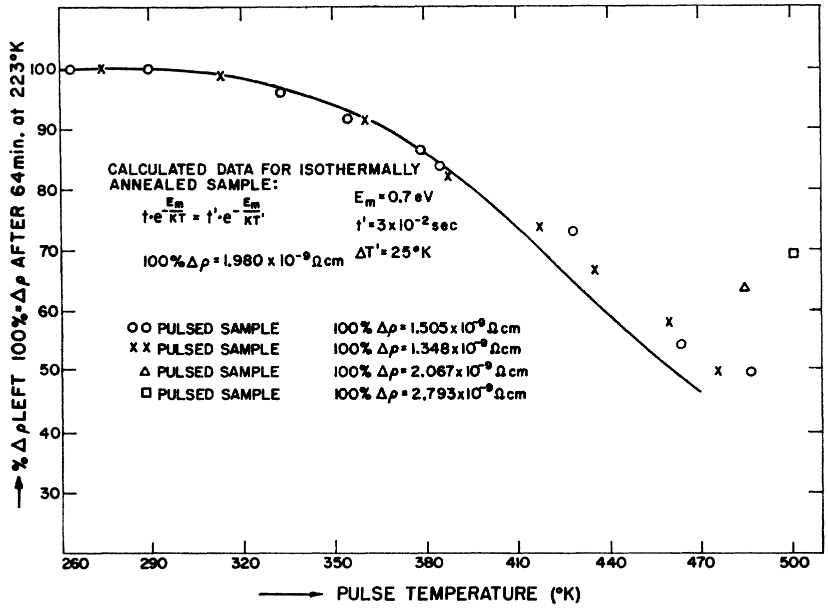

FIG. 3. Experimental results of pulsing. × × shows results for a copper specimen (initial $\Delta\rho = 1.348 \times 10^{-9}$ Ω cm) pulsed to a set of increasing temperatures as shown. ○ ○ gives results for another copper specimen (initial $\Delta\rho = 1.505 \times 10^{-9}$ Ω cm). △ was a copper specimen subjected to a single pulse to 485°K (initial $\Delta\rho = 2.067 \times 10^{-9}$ Ω cm). □ was another copper specimen subjected to a single pulse (initial $\Delta\rho = 2.793 \times 10^{-9}$ Ω cm). All pulses 3.0×10^{-2} sec. Solid curve shows theoretical prediction for $B_2 > 1.1$ eV for pulses to temperatures 25°K apart ($\Delta\rho = 1.426 \times 10^{-9}$ Ω cm initially).

where t is the time for the isothermal anneal, t' is the time for the pulse ($t' = 0.03$ sec), T is the temperature of the isothermal anneal, T' is the temperature of the pulse, and E_M is the energy of migration ($E_M = 0.7$ eV).

Using this equation and the data of a sample isothermally annealed in stage III, a pulsing experiment has been calculated; the results are shown as the solid line of Fig. 3. In this constructed experiment the temperature difference between each pulse was 25°K.

The solid calculated line represents the data that have been obtained from actual pulsing experiments rather well. In addition Fig. 3 gives the results of two specimens that have been pulsed to high temperatures (480 and 490°K) without having been subjected to any previous pulses.

Pulsing experiments were also carried out with specimens that have been irradiated with a total dose of 5.9×10^{16} p/cm^2; the results are given in Fig. 4. They can also be represented by stage-III-type annealing alone as can be seen from the congruence of the data with the calculated solid line. Because the observed recovery in stage III occurs by second-order kinetics, the annealing of these more heavily damaged samples occurs at lower temperatures than that of the samples shown in Fig. 3.

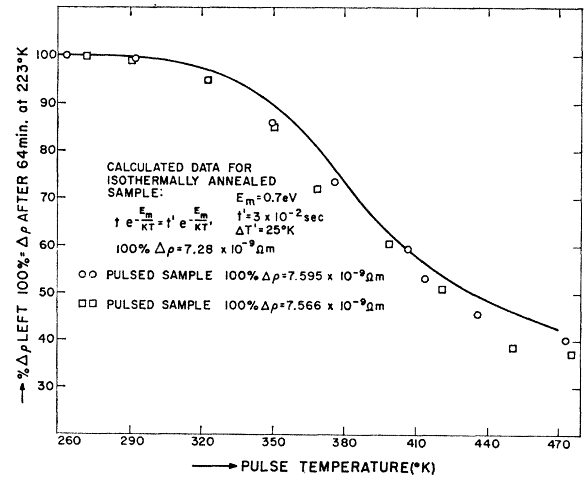

FIG. 4. Experimental results of pulsing. All pulses 3.0×10^{-2} sec. ○, initial $\Delta\rho = 7.595 \times 10^{-9}$ Ω cm. □, initial $\Delta\rho = 5.544 \times 10^{-9}$ Ω cm. Solid curve gives theoretical prediction for 25°K temperature increases (initial $\Delta\rho = 6.580 \times 10^{-9}$ Ω cm and $B_2 > 1.1$ eV).

A. Isothermal Step Annealing

Two specimens that were exposed to a total flux of 1.1×10^{16} p/cm^2 and two with a dose of 2.1×10^{16} p/cm^2 were isothermally annealed for 64-min periods at temperatures successively 20°K apart from 143 to 343°K. The experimental procedure and the calculation of the activation energy spectrum have been described in a previous paper.[1]

We have attempted to determine whether the annealing which occurs in the small peaks preceding the large peak (which obeys second-order kinetics) obeys first- or second-order kinetics. For the first-order kinetics we expect

$$d(\Delta\rho)/dt = -A(T)\Delta\rho \tag{5}$$

where $\Delta\rho$ is the damage resistivity. For second-order processes one should have

$$d(\Delta\rho)/dt = -B(T)\Delta\rho^2. \tag{6}$$

If one examines the experimental data given in our previous paper[1] together with the low-dose experiments considered here, one finds that the fractions of the total damage (a) annealing out in the small peaks (21.7% in the high-dose copper, 23.9% in the present low dose), (b) annealing out in the big peaks (50.0% in the high-dose copper, 45.8% in the present low dose), and (c) remaining at 30°C, stay essentially constant as the total damage is increased by a factor of 10. Thus, one finds that the concentration of the defects responsible for the small peaks has changed by a factor of about 10 when the dose changes by a factor of 10. If the annealing in the small peaks obeys first-order kinetics, we expect the corresponding annealing rates to change by a factor of 10. If, on the other hand, the annealing is by a second-order process, corresponding annealing rates should change by a factor of 100. Upon checking, one finds that corresponding annealing rates (i.e., annealing rates at the same point (*tT*) on the two isothermal curves) increases by a factor of 8.3 when the dose increases by a factor of 10. This factor is an average over the data taken at −110, −90, −70, and −50°C. For data taken in the big peak where previous work[1] has established second-order annealing kinetics, the rate of annealing changed by a factor of 40 on changing the dose by a factor of 10. Thus, in both cases the change in the annealing rate is not quite as large as one would expect. This indicates that not all of the $\Delta\rho$ is accounted

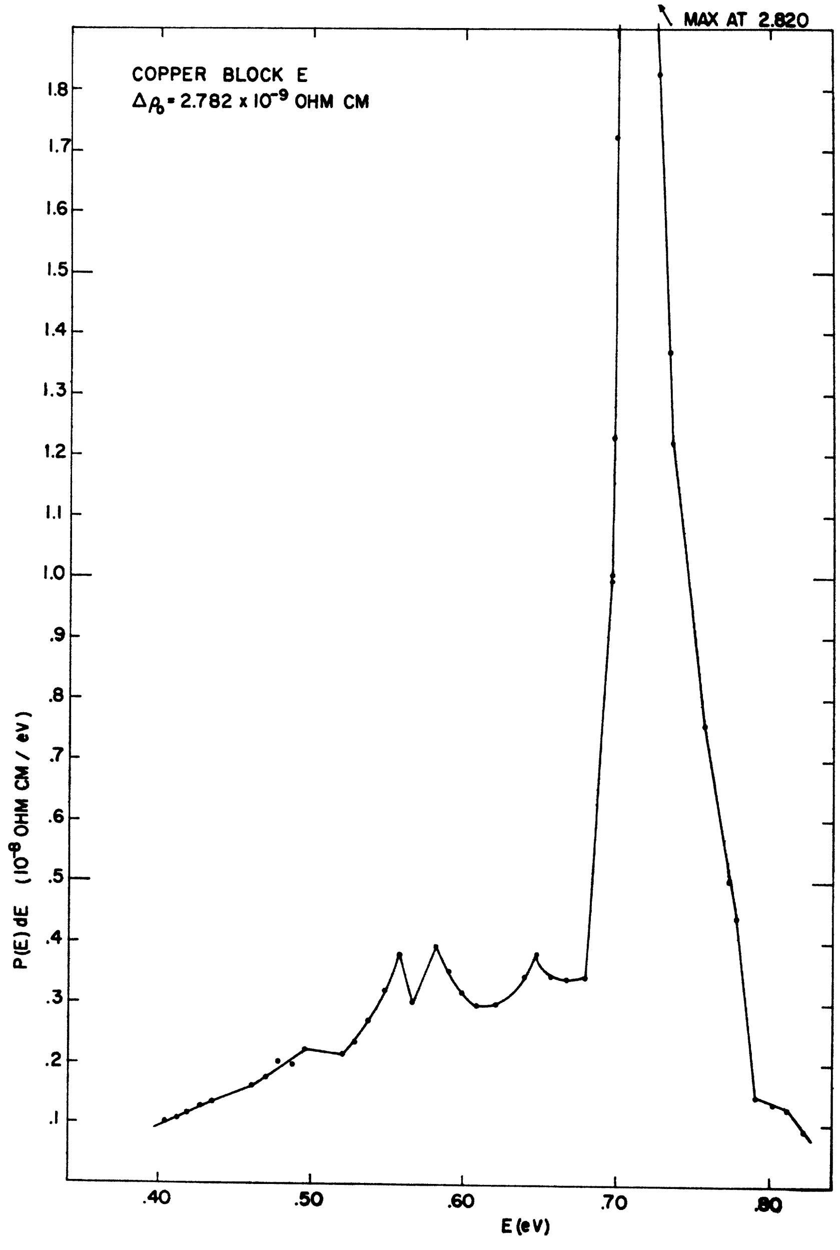

FIG. 5. The annealing spectrum of proton-irradiated copper. Low dose ($\Delta\rho_0 = 2.782 \times 10^{-9}$ Ωcm). First-order annealing with frequency factor $10^{11.6\pm0.5}$ if $E<0.69$ eV. Second-order with frequency factor 10^{18} if $E>0.69$ eV.

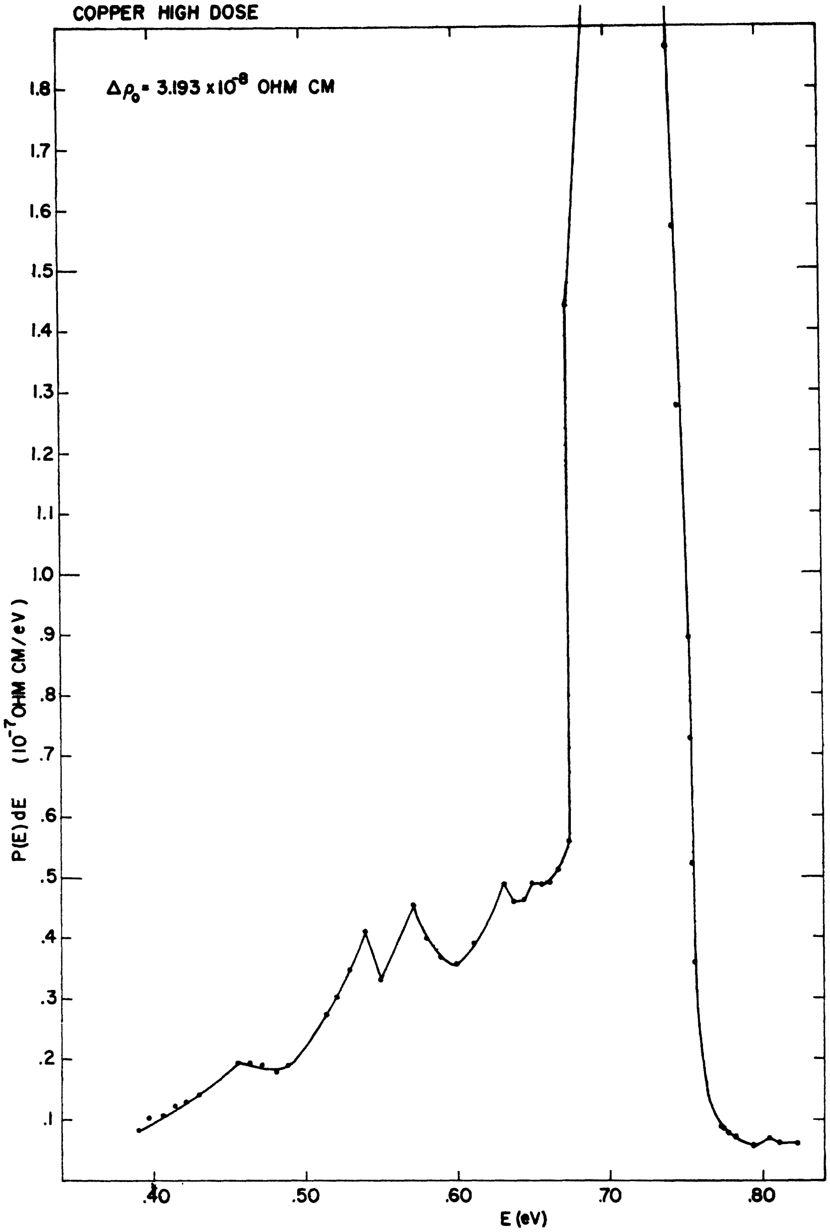

FIG. 6. The annealing spectrum of proton-irradiated copper. High dose ($\Delta\rho_0 = 3.193 \times 10^{-8}$ Ω cm). First-order annealing with frequency factor $10^{11.6}$ if $E < 0.69$ eV. Second order with frequency factor 10^{18} if $E > 0.69$ eV.

for by the defects which anneal out in the stage in question. Still the comparison demonstrates that the annealing below −30°C in copper obeys first-order annealing kinetics.

The annealing spectrum in the low-temperature region calculated assuming first-order annealing kinetics is shown in Fig. 5. The frequency factor required in the low-temperature region is $10^{11.6 \pm 0.5}$. Figure 6 shows the activation energy spectrum for the high-dose copper. The excellent agreement between the low dose spectrum and the high dose spectrum suggests that impurities are not important. Note also that the activation energy associated with the major stage III peak is also independent of dose. Figure 7 shows a similar annealing spectrum for silver. In this case, the frequency factor required in the temperature region below 243°K is $10^{12.3 \pm 0.5}$ (i.e., in the region which follows first-order annealing kinetics). Note that in silver there are no annealing peaks above the stage III peak but below 0.88 eV. This is in the range where one would expect to observe lattice vacancies. Figure 8 shows the annealing spectrum of gold. In gold, the first-order frequency factor is $10^{10.0 \pm 0.5}$.

V. ISOCHRONAL ANNEALS

The isochronal anneals were carried out by annealing the irradiated specimens for ten minute periods at suc-

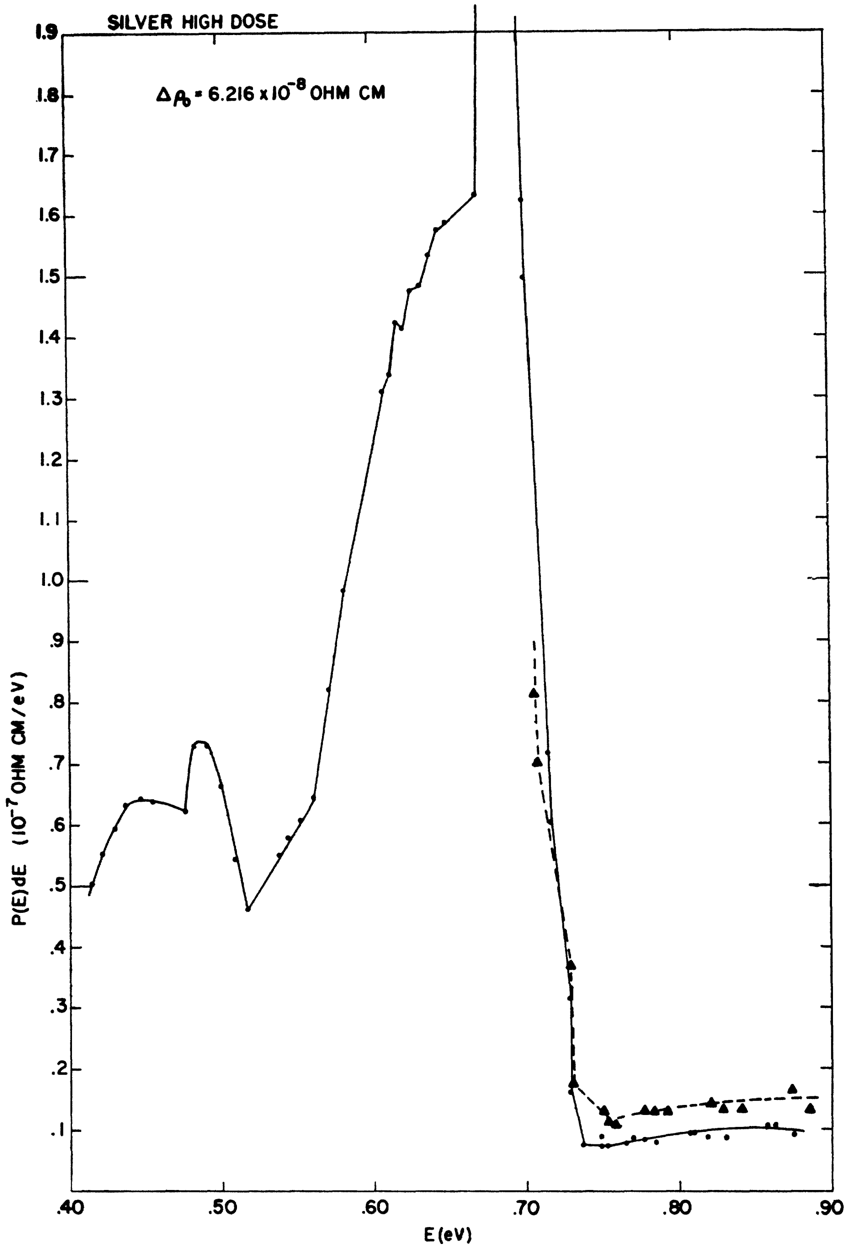

FIG. 7. The annealing spectrum of proton-irradiated silver. High dose ($\Delta\rho_0 = 6.216\times10^{-8}$ Ω cm). First-order annealing with frequency factor $10^{12.3}$ if $E < 0.67$ eV. Second order with frequency factor 10^{18} if $E > 0.67$ eV.

cessively higher temperatures. The temperature increment between successive anneals was 5°K and the resistivity decrease after each anneal was measured at liquid-helium temperature.

The annealing of one set of samples could only be started at a temperature of 188°K and one sample block could only be annealed up to a temperature of 210°K because of a mechanical failure of the apparatus. Therefore, none of these samples was annealed isochronally throughout the whole investigated temperature region. The results of both sample blocks have to be used in order to describe the annealing of the whole temperature interval and the dose dependence of the annealing processes cannot be investigated on the basis of these results.

Nevertheless, the curves which describe the annealing behavior at least qualitatively, show that several distinct annealing processes occur. The derivatives of these curves were calculated and are shown in Fig. 9. Four peaks can be distinguished at 160, 190, 200, and 260°K in these curves.

It is of interest that Martin[2] observed an annealing peak at 190°K in 99.999% pure copper irradiated at −196°C with 4-MeV electrons. His integrated flux was 3×10^{17} e/cm^2. Thus his damage was probably about 1.0×10^{-9} Ω cm, i.e., slightly less than our lowest damage.

---

[2] D. G. Martin, Phil. Mag. 6, 839 (1961).

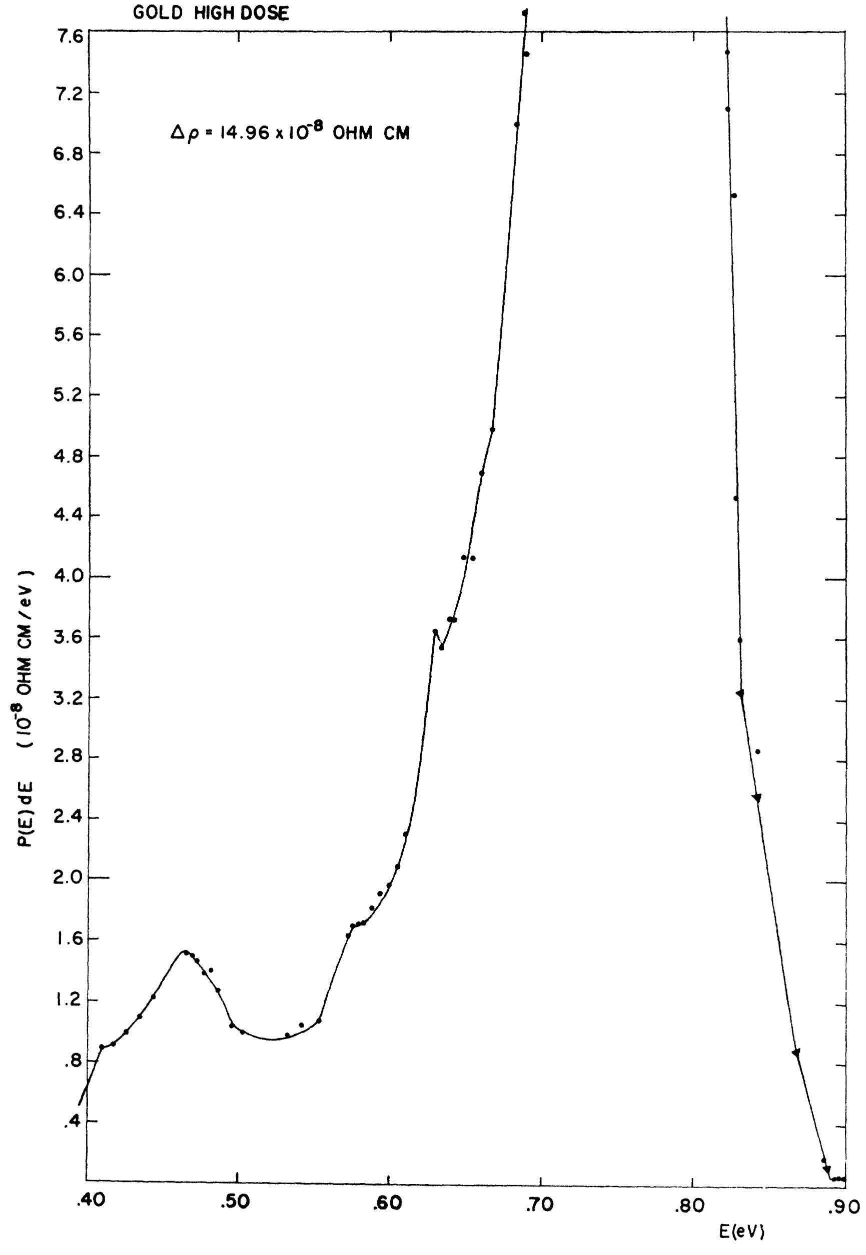

FIG. 8. The annealing spectrum of proton-irradiated gold. High dose ($\Delta\rho_0 = 14.96 \times 10^{-8}\ \Omega$ cm). First order with frequency factor 10^{10} if $E < 0.70$ eV. Second order with frequency factor 10^{18} if $E > 0.70$ eV.

VI. ISOTHERMAL ANNEALS

The order of reaction of a uniquely activated process can be determined from an isothermal annealing experiment. Two annealing processes were investigated by this method, i.e., the annealing of stage III and that occurring at 193°K.

Two samples that were irradiated to a total dose of 2.1×10^{16} p/cm^2 were isothermally annealed at 263°K for over 2000 min, and the decrease of resistivity with time was followed by taking the specimens out of the annealing bath and measuring the resistivity at liquid-helium temperature.

In previous experiments it has been observed that stage III annealing follows second-order kinetics. Consequently, the data were plotted as $1/\Delta\rho$ versus time, where $\Delta\rho = \rho - \rho_\infty$ and ρ_∞ is the asymptotic value of the isothermal annealing curve; the result is given in Fig. 10. In order to show the data up to 100 min more clearly these points are plotted on an expanded time scale. One can see very clearly that the data lie on a straight line except for times shorter than 16 min. It should be noted that the slopes of both straight lines are identical.

On the basis of the results of Fig. 10 stage III can be represented by a second-order process with a unique activation energy after about 40% of the damage has

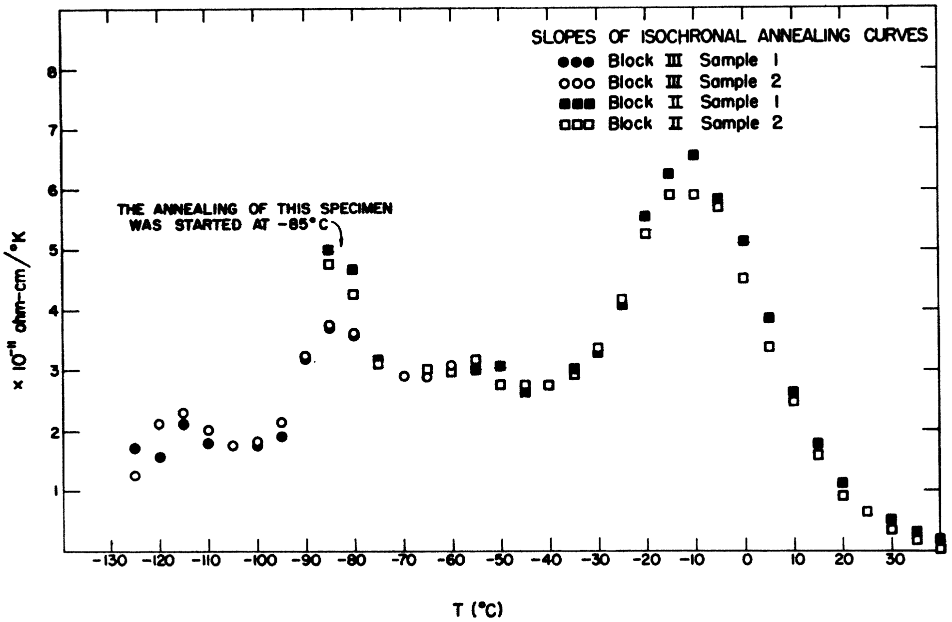

FIG. 9. The isochronal annealing of proton-irradiated copper. Each anneal was for ten minutes at temperatures 5°K apart.

annealed out. A similar result for stage III has been found by Bauer and Sosin[3] in electron-bombarded gold.

The annealing at $-80°C$ has been investigated by a similar experiment. Two samples that were irradiated with 5.9×10^{16} p/cm^2 have been isothermally annealed at $-82.34°C$ for 255 min and the decrease of resistivity with time was measured. Plotting the logarithm of $\Delta\rho$ versus the annealing time (see Fig. 11) one finds that two processes occur. From the difference in the two slopes their activation energies differ by 0.03 eV as they have the same frequency factor. Note that these results

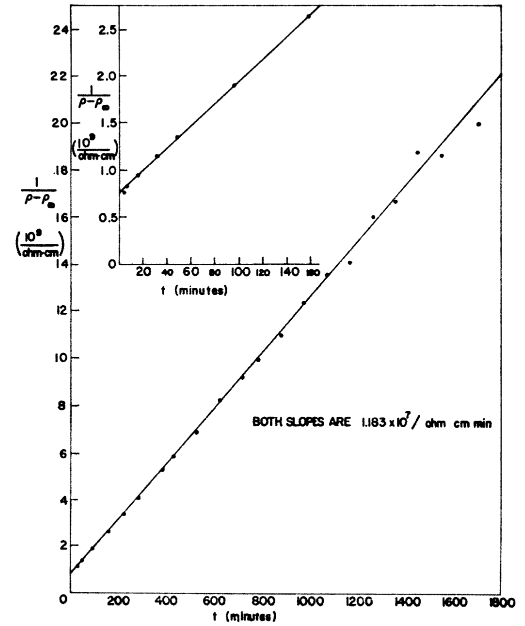

FIG. 10. Isothermal annealing of proton-irradiated copper. The samples were first annealed at $-50°C$ for 3h to eliminate the first-order processes. Then they were isothermally annealed at 263.0°K. Initially at 263.0°K, $\Delta\rho=4.750\times10^{-9}$ Ω cm.

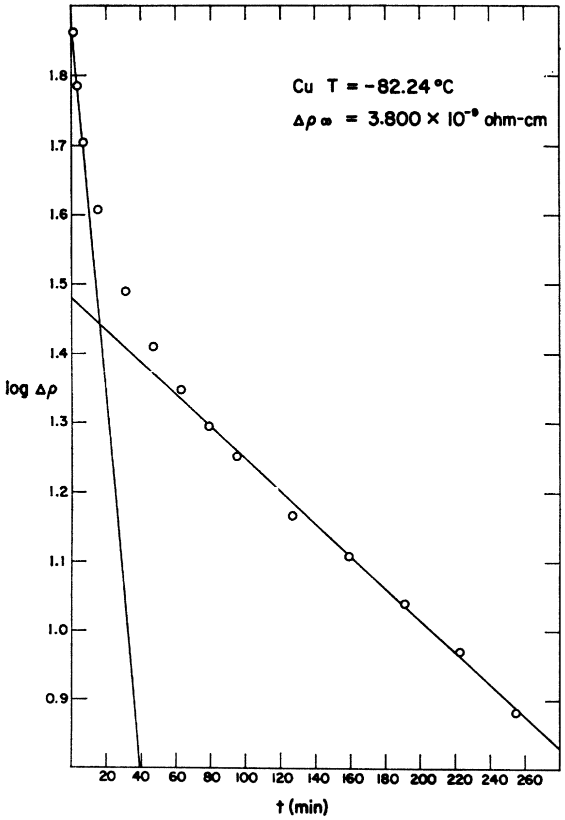

FIG. 11. Isothermal annealing of proton-irradiated copper at $-82.24°C$. Note the two first-order processes.

---

[3] W. Bauer and A. Sosin, Phys. Rev. **136**, A474 (1964).

are consistent with the fact that two first-order processes were found using the Primak analysis on the isothermal step annealing data.

VII. DISCUSSION

Thus far, three models have been suggested to explain stage III annealing. Let us consider each in turn and attempt to decide how well they fit the observed experimental facts.

The first model asserts that lattice vacancies move in stage III and that they anneal out at interstitial clusters or at interstitials trapped at impurities. This model does not fit the results found by Dworschak, Hershbach, and Koehler for copper and silver because the migration energies found in stage III disagree with the migration energy of a single vacancy. In copper from the activation energy for self-diffusion,[4] (i.e., 2.05±0.02 eV) and from the vacancy-formation energy observed by Simmons and Balluffi[5] (i.e., 1.17±0.11 eV), one finds that $E_M{}^V=0.88\pm0.13$ eV. This does not agree with the 0.71 eV found in stage III. The present experiments show that the 0.70±0.04 eV result holds when the amount of damage is varied by a factor of 10 (i.e., from $\Delta\rho\cong3\times10^{-9}$ to $\Delta\rho\cong3\times10^{-8}$ Ω cm). In the case of silver Doyama and Koehler[6] find that $E_M{}^V=0.83\times0.05$ eV. This disagrees with the result observed during stage III annealing of silver where one finds 0.67±0.03 eV. In gold, the situation is less certain. In gold the second-order process which occurs in stage III has an activation energy of 0.80±0.04 eV according to Dworschak, Herschbach, and Koehler and also according to Bauer and Sosin.[3] The activation energy for vacancy migration in gold is 0.83±0.04 eV so that vacancies could be involved. On the other hand, Venables and Balluffi[7] have observed shrinkage of vacancy tetrahedra in ion-bombarded gold when they annealed through stage III. Cotterill and Jones[8] did 3-MeV α irradiations on gold foils containing tetrahedra at room temperature. They found that the concentration of tetrahedra decreased with increasing α-particle dose. However, the tetrahedra vanished suddenly and did not shrink gradually. Since the vacancy tetrahedra should act as sinks for interstitials, the above experiments indicate that interstitials or interstitial clusters of some kind migrate at temperatures appropriate for stage III in gold. The vacancy tetrahedra are stable to about 450°C in unirradiated gold.

The second model, as described by Huntington,[9] claims that di-interstitials are formed during stage I annealing and that these migrate to lattice vacancies in stage III. The pulsing experiment reported in the present paper requires that if stage III results from the migration of di-interstitials then the binding energy of the di-interstitial must be larger than 1.0 eV in copper. This is possiple since the total formation energy of the di-interstitial is calculated to be 7 or 8 eV, so that a binding energy of 1.5 eV would correspond to a reduction of the total energy associated with the defect of about 20% which is not a large fraction.

Cooper, Koehler, and Marx[10] irradiated copper at 12°K using 12-MeV deuterons. They found that the resistivity remaining after an anneal to 133°K was about the same as that put in during an irradiation with the same integrated flux done at 133°K. For example for silver 10^{17} deuterons per cm^2 at 133°K gave $\Delta\rho=1.05\times10^{-7}\pm0.1\times10^{-7}$ Ω cm. If the irradiation was done at 12°K and the specimen was then annealed to 133°K, $\Delta\rho=1.125\times0.1\times10^{-7}$ Ω cm. Similar results were obtained for copper.

Corbett, Smith, and Walker,[11] however, find very different results using 1.4-MeV electron irradiation. They found that if pure copper is irradiated with 6×10^{17} e/cm^2 at 80°K, then $\Delta\rho=(2.1\pm0.05)\times10^{-10}$ Ω cm. If the sample is irradiated at 20°K and is annealed to 80°K, then $\Delta\rho=(6.1\pm0.2)\times10^{-10}$ Ω cm. Thus the amount of damage retained is larger by a factor of three if it is introduced at a low temperature. This suggests that the larger concentrations of mobile defects which occur during annealing in the sample irradiated at 20°K result in a larger production of stable complexes. In the samples irradiated at 80°K the concentrations of the partners which react to form the stable defects are always so low that not many complexes are formed. A possible reason a similar result is not seen after deuteron irradiation is that the damage clusters contain more displaced atoms than occur in a cluster in an electron irradiation specimen, so that most of the annealing after deuteron irradiation occurs within a single damage cluster, hence the local-defect concentrations are similar in a specimen irradiated at 133°K and in a sample irradiated at 12°K and then annealed to 133°K. Corbett, Smith, and Walker explained their difference in damage production by supposing that the interstitials which migrate in stage I can annihilate at vacancies or agglomerate forming interstitial clusters. They could not explain this difference by supposing that two kinds of noninteracting interstitials are generated upon irradiation. Neither of the latter mechanisms provides a situation in which the amount of damage remaining at 80°K is sensitive to the temperature at which the irradiation is performed (see below, however).

Since this difference in the rate of production is crucial, it is fortunate that other data exist which sub-

---

[4] S. M. Makin, A. H. Rowe, and A. D. Le Claire, Proc. Phys. Soc. (London) **B70**, 545 (1957).

[5] R. O. Simmons and R. W. Balluffi, Phys. Rev. **129**, 1533 (1963).

[6] M. Doyama and J. S. Koehler, Phys. Rev. **127**, 21 (1962).

[7] J. A. Venables and R. W. Balluffi, Phil. Mag. **11**, 1021 (1965); **11**, 1039 (1965).

[8] R. M. J. Cotterill and M. W. Jones, Phil. Mag. **10**, 535 (1964).

[9] H. Huntington, Am. J. Phys. **32**, 775 (1964).

[10] H. G. Cooper, J. S. Koehler, and J. W. Marx, Phys. Rev. **97**, 599 (1955).

[11] J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. **114**, 1460 (1959).

stantiate it. Meechan and Brinkman[12] irradiated copper at 80°K using 1.25-MeV electrons. After 2×10^{18} e/cm^2, the resistivity increase was 0.98×10^{-9} Ω cm (initial residual resistivity was 3.4×10^{-9} Ω cm.) Sosin[13] gives damage production in copper at 6°K produced by electron irradiation for various electron energies. If we extrapolate his straight line from 0.97 MeV to 1.25 MeV, the damage introduced at 6°K by 2×10^{18} e/cm^2 is 16.3×10^{-9} Ω cm. At 0.97 MeV, he finds that 83% of the damage anneals out in stage I. Therefore, the resistivity remaining after warming to 80°K in his sample irradiated with 2×10^{18} e/cm^2 at 6°K would be 2.77×10^{-9} Ω cm. (The initial residual resistivity in this specimen was 5×10^{-9} Ω cm.) Even if one assumes that the fraction of damage recovered is as high as that seen by Corbett, Smith, and Walker, i.e., 87.2%, the amount which remains after warming to 80°K, is 2.09×10^{-9} Ω cm, which is larger than the damage put in at 80°K by a factor of more than 2.

Sosin and Rachel[14] irradiated pure aluminum at 4.2°K using 1.1-MeV electrons. They state that 85% of the resistivity increment anneals out below 80°K. For 1.5×10^{18} e/cm^2 this would leave $\Delta\rho=20.5\times10^{-10}$ Ω cm after annealing to 80°K. Direct irradiation at 80°K introduces $\Delta\rho=13\times10^{-10}$ Ω cm after the same integrated flux. Hence, they observe qualitatively the same phenomena as those found by Corbett and Walker but the magnitude of the effect appears to be smaller for aluminum than for copper.

Concerning the possible influence of impurities on the difference between the electron damage production rate at 80°K and that observed upon irradiation at 20°K and on warmup to 80°K, Sosin and Rachel[14] have found that for aluminum plus 0.1 at.% zinc the damage introduced at 80°K agrees well with the amount of damage remaining after an irradiation of the alloy at 4.2°K with the same integrated flux and a subsequent warmup to 80°K. This result indicates that impurities, if they trap the migrating defect, tend to reduce the difference which we have been discussing.

To summarize, the results obtained after electron irradiation show that more damage remains if one irradiates at at temperature too low for stage I annealing and then anneals to above stage I, than if one gives the same irradiation above stage I. The evidence exists for aluminum and copper and evidence exists for both these materials that some defect migrates many atomic distances in stage I. Since most of this extra damage anneals in stage III, this suggests that one of the defects associated with stage III annealing is formed in stage I.

The third model described by Meechan, Sosin, and Brinkman[15] supposes that two kinds of interstitials are generated during irradiation. The metastable interstitial migrates in stage I, whereas the stable interstitial migrates in stage III. The pulsing experiments enable us to calculate a lower limit for the barrier which resists conversion of the stable interstitial into the metastable interstitial in copper (see Fig. 12). This barrier is sufficiently high that during a 30-msec pulse to 230°C, the migrating defect remains the stable interstitial (if we accept this model). Thus

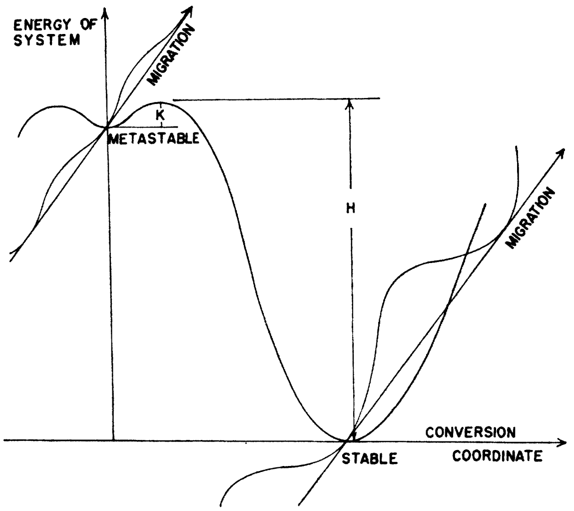

FIG. 12. Schematic diagram showing energy barriers for migration and conversion of a metastable interstitial and the energy barriers for the migration and conversion of a stable interstitial. The diagram assumes that appreciable concentrations of stable and metastable interstitials can exist simultaneously.

$$3\times10^{-2}\times10^{13}\times e^{-H/kT}<1\,,$$

where H is the barrier height and T is the absolute pulse temperature. Thus one finds that $H>1.14$ eV, so that the stable interstitial would be difficult to convert to the metastable interstitial.

The data of Corbett, Smith, and Walker[11] on the annealing of copper irradiated by a low dose of 1.4-MeV electrons at 20°K enable us to establish a lower limit on the barrier which resists conversion of the metastable interstitial into a stable interstitial. Corbett and Walker found that 3.3×10^{-11} Ω cm annealed out in stage I_E after a very light dose. The annealing obeys second-order kinetics. Therefore, since the initial concentration of migrating interstitials was about 1.6×10^{-7}, the number of jumps required to encounter another defect (i.e., a vacancy or another interstitial) was the reciprocal of $700\times1.6\times10^{-7}$ or about 1×10^4 (where we have used the Granato-Nilan[16] capture volume). During this 60-min anneal at 52.7°K, the migrating defect does not convert from metastable to stable. Therefore, the barrier height K resisting this conversion must be such that:

$$P_{\mathrm{conv}}/P_{\mathrm{jump}}\cong e^{-(K-E_M{}^{\mathrm{I}})/kT}\lesssim10^{-4}.$$

---

[12] C. J. Meechan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

[13] A. Sosin, Phys. Rev. **126**, 1698 (1962).

[14] A. Sosin and L. H. Rachal, Phys. Rev. **130**, 2238 (1963).

[15] C. J. Meechan, A. Sosin, and J. A. Brinkman, Phys. Rev. **120**, 411 (1960).

[16] A. V. Granato and T. G. Nilan, Phys. Rev. **137**, 1250 (1965).

Thus, $K \geq 0.162$ eV, so that the barrier restricting conversion from a metastable interstitial to a stable interstitial is greater than 0.16 eV in copper. ($E_M{}^{\mathrm{I}} = 0.12$ eV.)

Let us briefly examine again the three proposed models in an attempt to sum up. First, we considered vacancy migration to interstitial clusters as being responsible for stage III annealing. This was rejected because $E_M{}^{\mathrm{III}} \neq E_M{}^{\mathrm{V}}$. We have also attempted to rescue this model by supposing that the lattice strains near the interstitial clusters reduce the vacancy migration energy. In our calculations using both spherical and platelike clusters, we were unable to achieve a sufficiently large reduction (i.e., for copper from 0.88 eV down to 0.70 eV). In addition, a large enough reduction would have associated with it an appreciable spread in vacancy-migration energies. Therefore, stage III annealing is probably not a result of vacancy migration.

Consider next the two-interstitial model. The experiments of Corbett, Smith, and Walker, in which they find more damage at 80°K after an irradiation at 20°K and a warmup to 80°K than after the same integrated electron flux at 80°K, were taken to be evidence for the production of interstitial clusters by the attractive interaction of interstitials with one another. Moreover,[17] they also found that the amount of stage III annealing increases as the amount of damage remaining at 80°K increases. There is, however, another way to regard this evidence. Suppose that the interstitial which moves in stage I can be converted into a stage-III-type interstitial when it encounters another interstitial. It is possible that the highly inhomogeneous strain fields near an interstitial aid in the conversion. The Corbett-Smith-Walker experiments can then be as well understood by supposing that more damage is retained by irradiating at 20°K and warming than by irradiating at 80°K, because the conversion to immobile stage III interstitials is enhanced, since the necessary concentrations of the various interstitials is large in the first case. Thus, the Corbett-Smith-Walker experiments are not decisive. A real test would be to look for interstitial clusters using electron microscopy in a specimen which had been electron-irradiated. The examination should be made at a temperature below that giving stage III annealing. Such observations do not as yet exist. Makin, Whapham, and Minter[18] have examined copper at −50°C after neutron irradiation at 80°K. They found large dislocation loops and small defects about 25 Å or less in size. However, a pile neutron gives a primary displaced copper atom 20 keV or so, which could produce enough defects in a small region to give contrast in the electron microscope.

In conclusion, one must either find some reason for an alteration of the vacancy-migration energy or adopt one of the interstitial models for stage III annealing. The pulsing experiments place limitations on either of the models involving interstitials setting the binding energy of the di-interstitial above 1.0 eV and requiring a barrier larger than 1.14 eV for conversion of a stable to a metastable interstitial.

There is one further remark that should be made. Nilan and Granato[16] have shown that the stage I_E annealing peak in copper shifts in temperature with dose in a manner consistent with the second-order annealing kinetics. They also note that if the interstitial involved jumps only along one crystallographic direction, then one would expect third-order annealing kinetics. This would be the situation if a crowdion moves along its particular (110) direction. Seeger[19] has attempted to avoid this dilemma by supposing that the crowdion vacancy annealing will be a combination of first order for those crowdions which jump eventually to the vacancy from which they were generated and third order for the crowdions which are eliminated at other vacancies which are encountered in a random walk in one dimension. Granato[20] points out that such an explanation will not fit because any possible first-order processes (having a peak I_E which will not alter its position in temperature as the irradiation dose is altered), should show up in Corbett, Smith, and Walker's high-dose data as a peak at about 52.5°K. In other words, in this case there should be two peaks, one which stays fixed in temperature and another which is concentration-dependent and appears at lower temperature as the concentration increases. This is not observed. Therefore, if any first-order annealing does occur in stage I_E, it must be present to less than 5% of the total I_E damage. Note that Seeger agrees that crowdion migration would give third-order annealing kinetics. Therefore, the interstitial which migrates in stage I_E must execute a random walk in three dimensions.

APPENDIX

The pulsing circuit is shown in Fig. 13. It operates as follows: first switch S_1 (double-pole single-throw) is closed to charge the 30-μF and 4-μF condensors; then S_1 is opened. Second, switch S_2 is closed; this arranges matters so that when the thyratron fires causing relay R_1 to switch from position 1 to position 2 it will hold in position 2. Third, switch S_3 is closed. This begins the pulse by supplying a large current to the sample from the 18-V battery on the right. In addition, a constant current sufficient to hold the sample at the pulse temperature is furnished by the 18-V battery on the left. The large current is cut off after about a millisecond by the burning out of a copper fuse wire. Closing S_3 also throws relay R_3 from position 1 to 2 after a time delay

---

[17] R. M. Walker, *Proceedings of the E. Fermi International School of Physics*, edited by D. S. Billington (Academic Press, Inc., New York, 1962), p. 594.

[18] M. J. Makin, A. D. Whapham, and F. J. Minter, Phil. Mag. **6**, 465 (1961).

[19] A. Seeger, in *Symposium on Radiation Damage in Solids and Reactor Materials, Venice, 1962; Radiation Damage in Solids I* (International Atomic Energy Agency, Vienna, 1963), p. 203.

[20] A. Granato (private communication).

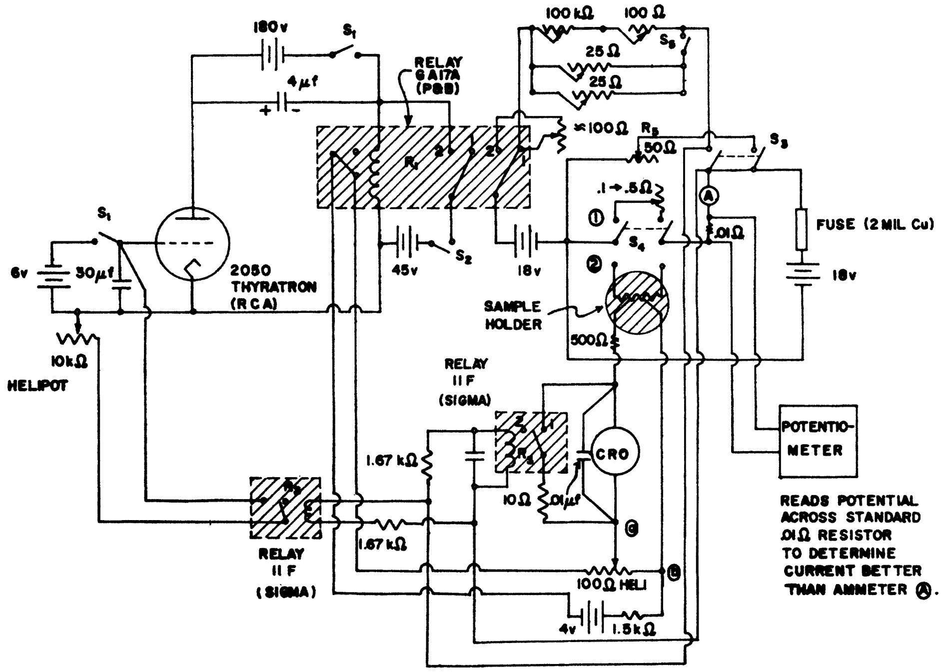

FIG. 13. Diagram of the pulsing circuit.

of from 1–4 msec. During this initial time delay the oscilloscope is shorted out through the 10-Ω resistor and hence the initial disturbances are not recorded. The oscilloscope is used to measure the voltage across the gauge length of the specimen.

Closing S_3 also activates relay R_2 which allows the 30-μF capacitor to discharge with a time constant determined by the 10 kΩ helipot. When the potential across the 30-μF capacitor is low enough, the thyratron fires causing relay R_1 to go from position 1 to 2. This inserts a large resistor (about 100 Ω) into the specimen circuit decreasing the specimen current by a large factor and thus ending the pulse.

In trial runs 0.6-mil-diam potential leads were spot-welded at various positions along the 5-mil-diam specimen to determine the temperature uniformity during a pulse. For the largest pulses (to 230°C), the temperature was constant within the gauge length to ±5°C. The pulse temperature was obtained by measuring the constant current using a dc ammeter and a matched dummy specimen in a separate experiment prior to the pulse. Then the voltage across the specimen during the pulse together with the current during the pulse gives the specimen resistance. Since the resistance of the specimen has been previously measured at 20°C, these observations suffice to give the specimen temperature. There is a slight error in the current because the matching is done at 20°C and the resistance of the hot (230°C) specimen is about twice as large as that of the cool (20°C) specimen. However this error is at most 3% because the resistance of the specimen is only a small fraction of the total resistance in the constant current circuit.

All of the circuit adjustments necessary for obtaining good matching of the capacitor current and the constant current, plus a knowledge of what temperature a given set of adjustments will attain for each specimen, are obtained by tests on the given specimen before irradiation, since the change in the room-temperature resistance of a sample upon irradiation is only a few tenths of a percent.