CHANGES IN MINORITY-CARRIER LIFETIME IN SILICON AND GALLIUM ARSENIDE RESULTING FROM IRRADIATION WITH 22- AND 40-MeV PROTONS

by Marvin E. Beatty

Langley Research Center
Langley Station, Hampton, Va.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • FEBRUARY 1969
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SUMMARY

Experiments were performed to examine the differences in the damage produced in n-type and p-type silicon and n-type gallium arsenide by irradiation with 22-MeV and 40-MeV protons. The parameter used to examine these differences was the minority-carrier lifetime in the base region of a photovoltaic p-n junction. From the data obtained, the relative merits of the three types of semiconductor material are compared in regard to their performance in a space radiation environment.

Results of the experiments indicate gross differences in reduction of minority carrier lifetime between the three materials. Gallium arsenide was least affected by radiation; p-type silicon was next. Curves and tables are presented to depict some differences between the materials.

It is concluded that gallium arsenide might be preferable to silicon in some devices to be subjected to a radiation environment. It was also found that 22-MeV protons produced a much higher degree of damage in silicon than 40-MeV protons did. The differences in damage produced were not so pronounced for gallium arsenide irradiated with protons of these two energies.

INTRODUCTION

Gallium arsenide (GaAs) is a III-V semiconducting compound with physical characteristics somewhat different from silicon (Si), as is shown in table I. Some of the differences in the physical characteristics of Si and GaAs render GaAs more adaptable to many types of semiconductor devices (e.g., microwave diodes, diode injection laser, and solar cells). Gallium arsenide is favorable for use in solar cells since it can operate in a

*The information presented herein was included in a thesis submitted in partial fulfillment of the requirements for the degree of Master of Arts in Physics, The College of William and Mary in Virginia, Williamsburg, Virginia, May 1966.
temperature range up to 300°C (as compared with 200°C for Si). It is also possible to achieve a higher photovoltage with GaAs (0.9 volt) than with Si (0.6 volt). (See ref. 1.)

It has been predicted that GaAs would be very resistant to radiation damage. Since the energy maximum in the valence band of GaAs lies in the same direction in wave vector or "k" space as the energy minimum in the conduction band (ref. 2), direct transitions of electrons from the valence band to the conduction band can be made. The lifetime for an electron in GaAs is very short (nanoseconds compared with microseconds in silicon) and would not be as strongly affected by low concentrations of radiation-produced recombination centers formed in the gap as the lifetime in silicon would.

Most of the radiation damage studies reported for proton damage to GaAs have been for low-energy protons (20 MeV or less, refs. 3 and 4). Based on energy-versus-damage studies for proton irradiation of silicon (ref. 5), most of the damage to semiconductor materials appears to occur with proton energies of about 50 MeV and below. In order to obtain a more complete understanding of radiation effects in GaAs for this energy range and to obtain a comparison of these effects between GaAs and Si, an investigation was initiated to study damage effects of proton energies between 5 and 50 MeV. The results of this investigation are presented in this report.

The minority-carrier lifetime, the average time that excess minority carriers (holes or electrons) will exist before they are reduced to a factor of 1/e of their original number as a result of the recombination process, is one of the more sensitive physical properties of most semiconductors to ionizing radiation, as can be pointed out by electron-bombardment studies (refs. 6 to 11). For this reason, the effect of proton damage on the semiconductor lattice of the materials was monitored by observing changes in the minority-carrier lifetime by an experimental procedure described in reference 12.

The 40-MeV proton irradiation was performed with the linear accelerator at the University of Minnesota and the 22-MeV proton irradiation, with the cyclotron at the Oak Ridge National Laboratory.

SYMBOLS

A sample area, cm²
D minority-carrier diffusion constant (holes or electrons), cm²/sec
Dp diffusion constant for holes, cm²/sec
E proton energy, MeV
$E_c$  conduction band, eV

$E_v$  valence band, eV

$f_r$  fraction of recombination centers occupied by holes or electrons

$g$  rate of generation of minority carriers by photons, cm$^{-3}$

$H$  absolute light energy density, watts/cm$^2$

$h\nu$  photon energy, where $h$ is Planck's constant and $\nu$ is frequency, eV

$I$  short-circuit current, A

$k$  wave vector in reduced Brillouin zone

$L$  diffusion length (holes or electrons), $\mu$m

$L_b$  diffusion length of minority carriers in base region, $\mu$m

$L_p$  diffusion length of holes, $\mu$m

$N_o$  equilibrium concentration of electrons

$N_r$  total concentration of recombination centers

$\Delta N$  number of electrons above equilibrium concentration

$P$  hole concentration

$P_0$  equilibrium concentration of holes

$\Delta P$  number of holes above equilibrium concentration

$R$  coefficient of reflection for wavelength $\lambda$, percent

$T$  temperature, $^\circ$C

$V_n$  thermal velocity for electrons, cm/$\mu$sec

$V_p$  thermal velocity for holes, cm/$\mu$sec
\( X \) distance into crystal, \( \mu m \)

\( \alpha \) absorption coefficient for wavelength \( \lambda, \text{cm}^{-1} \)

\( \lambda \) wavelength, \( \mu m \)

\( \sigma_n \) capture cross section for electrons, \( \text{cm}^2 \)

\( \sigma_p \) capture cross section for holes, \( \text{cm}^2 \)

\( \tau \) minority-carrier lifetime (holes or electrons), \( \mu \text{sec} \)

\( \tau_1 \) lifetimes of minority carriers from several energy levels, \( \mu \text{sec} \)

\( \tau_n \) lifetime for electrons in p-type material, \( \mu \text{sec} \)

\( \tau_o \) lifetime before irradiation (holes or electrons), \( \mu \text{sec} \)

\( \tau_p \) lifetime for holes in n-type material, \( \mu \text{sec} \)

\( \phi \) proton fluence, \( \text{p}^+/\text{cm}^2 \)

Notations:

e\(^{-}\) electron

GaAs gallium arsenide

Ge germanium

In indium

n-p n-type material (surface layer) on p-type material (base)

n-type material with an excess of electrons

O\(_2\) oxygen

p-n p-type material (surface layer) on n-type material (base)

p\(^{+}\) proton
APPARATUS AND PROCEDURE

The method of observing change in minority-carrier lifetime (ref. 12) utilizes a monochromatic infrared light source (with a wavelength of 1.0 µm for Si and of 0.9 µm for GaAs) to generate a current in the base of a p-n junction photovoltaic device (solar cell). The current obtained is used to determine the diffusion length by utilizing an equation developed in reference 12:

\[ \frac{1}{L_b} = \alpha \left[ \frac{AH(1 - R)}{(h\nu)I} - 1 \right] \]

The dependence of \( \tau \) in silicon on the number of recombination centers introduced is presented in appendix A. The equation used to relate \( L \) to \( \tau \) is derived in appendix B and is

\[ \tau = \frac{L^2}{D} \]

where \( D \) is the minority-carrier diffusion coefficient for the material and is assumed to be constant for all fluences. A more complete discussion of the theory of the minority-carrier lifetime may be found in appendix A and references 12 and 13.

The procedure used to determine \( \tau \) and its changes due to proton bombardment involved a determination of \( L \) at various proton fluences by utilizing the experimental method previously described. Measurements of \( H \) and \( I \) made at each fluence point were used to calculate \( \tau \).

The sample carriage used for the 40-MeV proton experiment is shown in figure 1. The plate has provisions for holding 12 samples with electrical connections available for remote readout. Since the carriage can be moved both horizontally and vertically by remote control, the samples can be placed in the beam without cutting the accelerator off; thus the stability of the machine is maintained.

For the irradiation experiment at the Oak Ridge National Laboratory, a chamber was designed which holds 12 samples (fig. 2). The samples are mounted on connectors and extend to the center of the beam window. The entire assembly can be operated in air, vacuum, or any gaseous atmosphere desired. The samples are insulated and connected through a rotary commutator to remote electronic gear. The wheel is provided with heat
sinks, a sample locator, and a Faraday cup. Figure 3 shows the chamber connected to the proton beam pipe.

The proton fluence striking the Si and GaAs samples was monitored with an ion chamber using air as the gas. The output of the ion chamber was calibrated by the results of several iron-foil activation-analysis measurements at the Oak Ridge National Laboratory.

For the irradiation experiment at the University of Minnesota, the activation-analysis method was not available. Therefore, the ion chamber was calibrated by a Faraday cup. The Faraday cup is one of the simplest methods for determining the intensity of radiation particles. It consists essentially of a thick brass plate which completely stops the beam. The plate has electrical connections to an ammeter so that the current generated in the plate by the radiation is measured. This measure of incident charge from the radiation particles is displayed on a current integrator. The number of secondary emissions was suppressed electrostatically by evacuating the Faraday cup until it had a potential of a few hundred volts. The length of the cup was large compared with the diameter of the entrance aperture to form a small solid angle for escape of the secondary electrons.

The experimental procedure to determine radiation-induced changes in \( \tau \) was the same for both proton machines. Sample irradiation was controlled with a metal gate or shutter. The desired flux, of the order of \( 2 \times 10^9 \) protons/sec for 22 MeV and approximately \( 1 \times 10^{10} \) proton/sec for 40 MeV, was established by monitoring the current induced in the closed gate. The gate was then opened and the proton beam was allowed to pass through the ion chamber and strike the sample. When the current collected in the ion chamber indicated that the sample had been exposed to the desired proton fluence, the gate was closed and the change in the minority-carrier lifetime was determined after sufficient time had elapsed for transitory effects to disappear. This cycle was repeated until the sample had been exposed to all the desired fluences.

The temperature of the samples was monitored by using a thermocouple and was maintained at \( 28^\circ \pm 2^\circ \) C during irradiation.

The samples used in the experiments were commercial n-p and p-n Si solar cells. The resistivity of these samples ranged from 1.0 to 5.0 ohm-cm. The GaAs samples were an experimental p-n type. The n-type GaAs had a carrier concentration of approximately \( 7.3 \times 10^{17} \) e\(^{-}/\)cm\(^3\) and a resistivity of 0.0032 ohm-cm. The material was a single crystal cut in the 1:1:1 plane and doped with Ge. The junction was formed approximately 0.5 \( \mu \)m below the surface by diffusing in a mixture of 40 percent Zn and 60 percent In at \( 720^\circ \) C for 10 minutes. An analysis by the vendor showed that the major impurities in the GaAs were silicon and germanium which act as donors (ref. 2). Other impurities
which were detected, but which had a concentration less than 0.25 part per million ($<10^{16}$ cm$^{-3}$), were boron, fluorine, magnesium, aluminum, phosphorus, calcium, iron, chlorine, potassium, indium, and zinc. The techniques used to fabricate these samples may be found in references 14 and 15.

**EXPERIMENTAL RESULTS**

**Irradiation With 22-MeV Protons**

**Silicon.**—A large difference exists in the reduction of minority-carrier lifetime $\tau$ in n-type and p-type Si. This reduction in n-type and p-type Si irradiated with 22-MeV protons is presented in figure 4 where the ratio of minority-carrier lifetime to lifetime before irradiation is plotted as a function of proton fluence. The degradation in $\tau$ depicts a rapid introduction of damage centers. For all practical purposes, both materials are destroyed at $\phi \geq 10^{11}$ p$^+$/cm$^2$, since $\tau$ is so short that practical application could not be achieved. Thus, devices constructed of either type of Si would be subject to complete failure in this fluence region.

The reduction rate of $\tau$ in p-type Si is approximately $2^{1/2}$ times less than that in n-type at $\phi < 10^{11}$ p$^+$/cm$^2$. For $\phi > 10^{11}$ p$^+$/cm$^2$, there is a saturation effect caused by the density of defect centers produced within the crystal. Any free minority carriers produced by photon generation are quickly captured by the defect centers and recombine with majority carriers with a resultant reduction in $\tau$.

In n-type Si, oxygen impurities can lead to a large production of A-centers ($O_2$-vacancy complex) upon irradiation and then produce an acceptor level at $E_C - 0.45$ eV. Donor impurities such as phosphorus can contribute to the creation of E-centers (donor-vacancy complex) upon irradiation and produce an acceptor level at $E_C - 0.45$ eV.

Impurities also exist in p-type Si which produce significant donor levels upon irradiations at $E_V + 0.28$ eV and $E_V + 0.05$ eV. (See ref. 16.) However, the capture cross section for the defects produced in n-type Si is larger than the capture cross section for defects in p-type Si.

**Gallium arsenide.**—Figure 4 also presents typical $\tau$ changes in n-type GaAs irradiated with 22-MeV protons. Gallium arsenide is shown to experience much less reduction in $\tau$ than either type of Si. A reduction of less than 20 percent occurs up to $\phi = 10^{12}$ p$^+$/cm$^2$. For both types of Si, the reduction in $\tau$ at $\phi = 10^{12}$ p$^+$/cm$^2$ is more than 90 percent. Above $\phi \approx 5 \times 10^{12}$ p$^+$/cm$^2$, $\tau$ in GaAs decreases rapidly with a slope similar to that for p-type Si. Therefore, GaAs is not invulnerable to proton bombardment, but the $\phi$ required for breakdown is about three orders of magnitude higher than that for Si.
Irradiation With 40-MeV Protons

Silicon.- The effect on n-type and p-type Si irradiated with 40-MeV protons is shown in figure 5. A rapid reduction of damage centers is exhibited by the linear slope of the curves, but the degradation of the minority-carrier lifetime is not as great as it is with 22-MeV proton irradiation. Therefore, the damage cross section for Si is not as great for 40-MeV protons as it is for 22-MeV protons. However, the reduction rate of \( \tau \) is still severe for 40-MeV protons and would render silicon devices useless when exposed to \( \phi \geq 1 \times 10^{12} \text{ p}^+/\text{cm}^2 \).

Gallium arsenide. - A typical plot of 40-MeV damage in GaAs is also presented in figure 5. The reduction in \( \tau \) up to \( \phi = 10^{12} \text{ p}^+/\text{cm}^2 \) is less than 10 percent; beyond this point \( \tau \) begins to decrease as rapidly as it did for 22-MeV protons, and the slopes for the two energies are very similar.

A comparison of the three semiconductor materials reveals that GaAs experiences no reduction in \( \tau \) until \( \phi \approx 5 \times 10^{11} \text{ p}^+/\text{cm}^2 \) where \( \tau \) begins to decrease slowly. Both types of Si experience larger changes in \( \tau \).

Comparison of 22-MeV and 40-MeV Proton Damage

The data in table II give an indication of the repeatability of \( \tau \) from sample to sample as well as of the production of defects in Si and GaAs irradiated with 22- and 40-MeV protons. The differences in damage produced by the two energies to the three semiconductor materials can be seen.

Figure 6 compares damage in n- and p-type Si irradiated with both 22- and 40-MeV protons and shows that p-type Si was damaged less than n-type at both energies. Both types of Si are damaged more with 22-MeV proton bombardment than with 40 MeV. For example, for p-type Si at \( \phi = 1 \times 10^{10} \text{ p}^+/\text{cm}^2 \), \( \tau \) is reduced by 35 percent with 22-MeV protons but by only 20 percent with 40-MeV protons. At the same fluence, \( \tau \) in n-type Si was reduced by 65 percent and 35 percent, respectively, with 22-MeV protons and 40-MeV protons.

Figure 7 shows that the difference in damage produced in GaAs irradiated with 22- and 40-MeV protons is small. However, 22-MeV protons are slightly more damaging than 40-MeV protons; this signifies some small effect of proton energy dependence in producing defects in GaAs. The major difference between the two energies occurs for fluences up to \( 5 \times 10^{12} \text{ p}^+/\text{cm}^2 \); above this fluence, \( \tau \) decreases rapidly and the damage produced by the two proton energies is almost the same.
DISCUSSION

From a comparison with Si, GaAs may be considered to be only slightly affected by exposure to proton energies of 22 MeV or higher. A proton fluence greater than $10^{13} \text{ p}^+ / \text{cm}^2$ is not usually encountered during the serviceable lifespan of semiconductor devices used on satellites, and the reduction in GaAs for $\phi$ below this level is less than 20 percent. The space radiation environment can be obtained by the use of reference 17.

The large reduction in the current output of the GaAs material, which is depicted as a corresponding reduction in $\tau$, is difficult to explain. Since the initial minority-carrier lifetime of the material and the distance a current carrier will diffuse are very short, it would not be expected that the radiation-produced defect centers would have much effect on $\tau$. The reduction in $\tau$ must be attributed to either of the following factors:

1. Recombination centers which are effective in competing with the transitions of minority carriers across the band gap

The GaAs damage mechanism could possibly be the formation of a donor-vacancy complex, since donor atoms are usually the impurities present in the largest amounts. This damage would be bulk and not surface as was found in reference 3 for proton energies less than 10 MeV.

2. A change in the diffusion constant $D$ at very high fluences

An investigation at the Langley Research Center has found that in germanium, $D$ increases when $\phi \geq 10^{11} \text{ p}^+ / \text{cm}^2$ for 22-MeV protons. This increase would lead to a reduction in carrier mobility and lifetime. It seems highly probable that this is a contributing damage mechanism for $\phi \geq 10^{12} \text{ p}^+ / \text{cm}^2$ in GaAs.

The actual damage observed is probably a combination of (1) and (2).

CONCLUSIONS

Experiments were performed to examine the differences in damage produced in n-type and p-type silicon and n-type gallium arsenide by irradiation with 22-MeV and 40-MeV protons. The parameter used to examine these differences was the minority-carrier lifetime in the base region of a photovoltaic p-n junction. From the data obtained, the following conclusions may be stated:

1. Gallium arsenide experiences much less reduction in minority-carrier lifetime than silicon when irradiated with either 22-MeV or 40-MeV protons.

2. p-type silicon is more radiation resistant than n-type.
3. At very high proton fluences \( (\geq 5 \times 10^{12} \text{ protons/cm}^2) \), however, gallium arsenide does experience a large reduction in minority-carrier lifetime for both 22-MeV and 40-MeV proton bombardment. When this reduction occurs, the slope of the lifetime-fluence curve is very similar to that of p-type silicon but with a proton fluence three orders of magnitude higher.

4. Comparisons of damage produced between the three materials irradiated with 22-MeV and 40-MeV protons indicate that 22-MeV proton effects are much more severe in silicon than 40-MeV proton effects. This is expected since the lower energy protons have a higher probability of displacing a silicon nucleus. The differences are much less noticeable in gallium arsenide, which means that energy-dependent radiation damage does not occur until much lower proton energies. This could mean that gallium arsenide experiences more surface damage than bulk damage.

Further work is necessary in order to form definite conclusions as to the type of damage mechanisms present in irradiated gallium arsenide.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., November 16, 1968,
124-09-12-09-23.
APPENDIX A

MINORITY-CARRIER LIFETIME THEORY

The Shockley-Read theory (ref. 18) gives the basic formulas for the recombination of excess minority carriers in silicon. According to this theory, energy levels localized deep in the forbidden gap will govern the recombination process. The lifetime $\tau$, when more than one energy level is present, is given by

$$\tau^{-1} = \sum_i \tau_i^{-1}$$

where $\tau_i$ is the lifetime due to each level. Thus, when ionizing radiation induces energy levels in the forbidden gap, the lifetime which is measured will be a statistical sum of the lifetimes due to each level.

Minority-carrier capture is usually a rate-limiting part of the recombination process for radiation-induced centers. An example is the rate of decrease of holes in n-type material expressed by

$$-\frac{d}{dt} \Delta P = \sigma_p V_p N_r f_r \Delta P$$

where

- $\Delta P$ concentration of holes in excess of equilibrium concentration
- $\sigma_p$ cross section for hole capture by center containing an electron
- $V_p$ thermal velocity for holes
- $N_r$ total concentration of type of recombination center being considered
- $f_r$ fraction of centers occupied by electrons (the fraction that may attract holes and capture them)

The hole lifetime becomes

$$\tau_p = \frac{\Delta P}{-\frac{d}{dt} \Delta P} = \frac{1}{\sigma_p V_p N_r f_r} \quad (1)$$
APPENDIX A

The foregoing expressions apply to recombination only when the defect level lies in the upper half of the band gap. If this is not the case, then the hole can escape to the valence band before the electron arrives to annihilate it.

The same type of equations will apply to electrons for levels created in the bottom half of the band of p-type material, but the terms in equation (1) will be for electrons instead of holes. Both hole and electron recombination equations may be combined into one recombination equation as follows:

\[
\tau = \frac{\tau_p (\Delta N + N_0) + \tau_n (\Delta P + P_0)}{N_0 + P_0}
\]  

where

\(N_0, P_0\) equilibrium concentration of electrons and holes, respectively

\(\Delta N, \Delta P\) number of electrons and holes, respectively, above equilibrium concentration

and where

\[
\tau_p^{-1} = \sigma_p V_p N_r \quad \text{(For holes)} \quad (3)
\]

\[
\tau_n^{-1} = \sigma_n V_n N_r \quad \text{(For electrons)} \quad (4)
\]

It is easily seen from equations (3) and (4) that the minority-carrier lifetime is inversely proportional to recombination-center concentration, since \(\sigma_p\) and \(V_p\) are essentially constants. Thus, a measurement of the minority-carrier lifetime at various proton fluences will yield a direct indication of the number of recombination centers being introduced. These measurements must be made after all transitory effects have decayed. Also, it is assumed that radiation-induced centers which are primarily traps do not reduce lifetime.

For gallium arsenide, the Shockley-Read recombination would not be important until extremely large numbers of defects are introduced in the gap.
APPENDIX B

RELATIONSHIP BETWEEN LIFETIME AND DIFFUSION LENGTH OF MINORITY CARRIERS

A definite relationship exists between diffusion length L and minority-carrier lifetime τ. For a uniform excitation, such as a monochromatic beam of infrared light, carriers are produced in a semiconductor deep in the material and thus surface effects are minimized. The steady-state density of the carriers produced is measured as a function of distance from the injection point. The lifetime is determined from the steady-state solution of the diffusion equation

\[
\frac{dP}{dt} = -\frac{P}{\tau} + D_p \nabla^2 P + g
\]  

(For holes) (5)

where

\begin{align*}
g & \text{ rate of generation of holes} \\
P & \text{ hole concentration} \\
D_p & \text{ diffusion constant for holes}
\end{align*}

After time has elapsed, the rate of carrier buildup due to g will cease, and a steady-state condition will exist. Then

\[
\frac{dP}{dt} = g = 0
\]

and

\[
-\frac{P}{\tau} + D_p \nabla^2 P = 0
\]

Equation (5) becomes manageable, being second order in P, and is written

\[
P = \tau D_p \frac{d^2 P}{dx^2}
\]  

(6)

The form for linear geometry which determines the number of carriers at length X is

\[
P = P_0 e^{-X/L_p}
\]  

(7)
APPENDIX B

Substituting equation (7) into equation (6) gives

\[ P_{0e}^{-X/L_p} = \frac{\tau D_p}{L_p^2} P_{0e}^{-X/L_p} \]

and

\[ L_p^2 = \tau D_p \]

Thus, it can be seen that the diffusion length and lifetime are directly related through a constant \( D \), which is known for most materials. If \( L \) is found, \( \tau \) can be determined for holes or electrons by

\[ \tau = \frac{L^2}{D} \]

The equation for determining \( L \) is derived in reference 12 and is

\[ \frac{1}{L} = \alpha \left[ \frac{A H (1 - R)}{(h \nu I)} - 1 \right] \]
REFERENCES


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TABLE II. - POST-BOMBARDMENT MINORITY-CARRIER LIFETIMES IN SILICON AND GALLIUM ARSENIDE
Figure 1.- Sample carriage used for 40-MeV proton experiment.
Figure 3: Bombardment chamber connected to the 22-MeV proton beam pipe.
Figure 4.- Minority-carrier lifetimes in typical samples of n-type silicon, p-type silicon, and n-type gallium arsenide irradiated with 22-MeV protons.
Figure 5.- Minority-carrier lifetimes in typical samples of n-type silicon, p-type silicon, and n-type gallium arsenide irradiated with 40-MeV protons.
Figure 6.- Minority-carrier lifetime in typical samples of n-type and p-type silicon irradiated with 22-MeV and 40-MeV protons.
Figure 7.- Minority-carrier lifetime in typical samples of n-type gallium arsenide irradiated with 22-MeV and 40-MeV protons.
"The aeronautical and space activities of the United States shall be conducted so as to contribute... to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—National Aeronautics and Space Act of 1958

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