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Charged Impurity Effects on the Deformation of Dislocation-Free Germanium*

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Acceptor or donor impurities in the concentration range $10^{19}/\text{cm}^3$ have a marked influence on the deformation behavior of germanium. Gallium raises the upper yield stress σ_M, while arsenic lowers it, in comparison with the value for undoped germanium. The behavior of σ_M is a direct consequence of the variation of dislocation velocity with doping. Direct measurements of dislocation velocity show that doping with arsenic raises dislocation velocity, while gallium lowers it, compared with the velocities for intrinsic germanium. The change in velocity or σ_M is not observed until the impurity concentration is comparable to the intrinsic carrier concentration at the test temperature. Neutral impurities in the range of $10^{19}/\text{cm}^3$ do not influence either σ_M or dislocation velocity. The net change in the σ_M or velocity parameters over the intrinsic values increases with decreasing temperature of test. From the dependence of dislocation velocity and maximum stress on impurity concentration, it appears that these parameters which control the deformation behavior are directly related to the electronic properties of germanium.

INTRODUCTION

THE electrical effects of dislocations in germanium have been investigated by many authors. In particular, the influence of dislocations on the conductivity and mobility of charge carriers has received special attention. There has, however, been no previous detailed report of the effect of electrically active impurities on the mechanical behavior of germanium. Previous work[1] with acceptor or donor concentrations in the range 10^{17}–$10^{18}/\text{cm}^3$ revealed no effect on the deformation behavior. It is the purpose of this work to show the rather large and unexpected effects of *p*- and *n*-type impurities on the behavior of dislocations introduced during mechanical deformation. The effects appear only when the impurity concentration becomes comparable with the intrinsic carrier concentration at the test temperature.

EXPERIMENTAL

Dislocation-free crystals heavily doped with arsenic or gallium were prepared from the melt by the Czochralski technique. Arsenic-doped crystals were grown in an argon atmosphere, while doping with gallium was carried out either in an argon ambient or vacuum. As in the case of intrinsic crystals of germanium,[2] the ambient in which these crystals were grown had no effect on the deformation characteristics. The maximum arsenic concentration incorporated into the dislocation-free crystals was about $2\times10^{19}/\text{cm}^3$. Whereas gallium-doped crystals with impurity concentrations of about $10^{20}/\text{cm}^3$ could be grown free of dislocations. All the crystals were grown in the orientation shown on the stereographic triangle Fig. 1. Prior to cutting the crystals were examined for dislocations by the etch pit technique, on a long {111} face parallel to the growth axis. In general the doped crystals were dislocation-free for about the initial 80% of their length. Etching with CP-4 revealed impurity striations perpendicular to the growth axis of the crystals. Similar striations have also been observed in silicon crystals and have been correlated with fluctuations in impurity concentration. Since the segregation coefficients of gallium and arsenic in germanium are less than unity, the impurity concentration also varied along the length of the crystal.

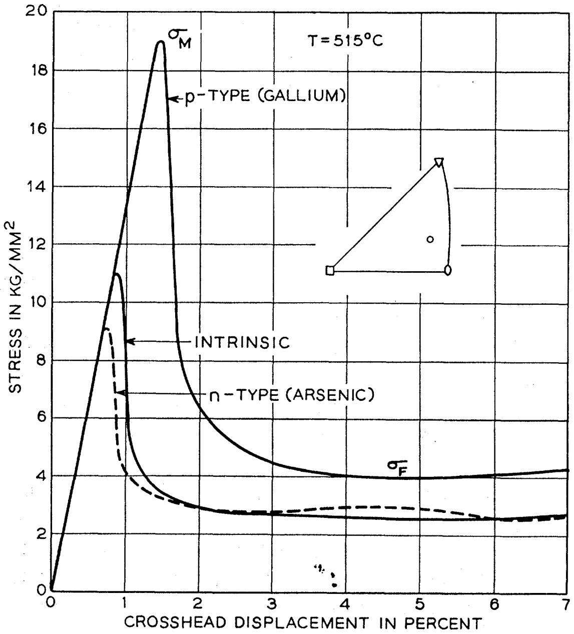

FIG. 1. Effect of *p*- and *n*-type impurities on the stress-strain behavior of dislocation-free germanium $T=515°\text{C}$. Crosshead velocity 0.005 cm/min.

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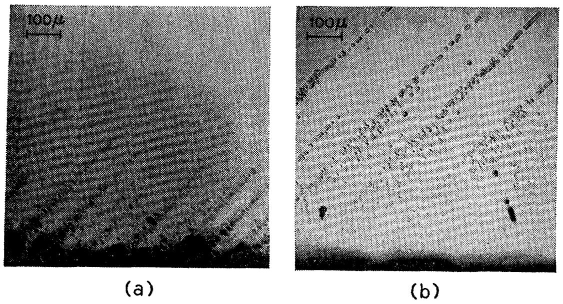
* Most of the experiments were performed while the authors were associated with Raytheon Research Division, Waltham, Massachusetts.

[1] J. R. Patel and B. H. Alexander, Acta Met. 4, 385 (1956).

[2] J. R. Patel and A. R. Chaudhuri, J. Appl. Phys. 34, 2788 (1963).



(a) (b)

FIG. 2. Dislocation motion from a scratch. (a) Gallium ($2\times10^{19}/\text{cm}^3$). $\tau_M=4$ kg/mm^2 stressed for 50 sec. (b) Arsenic ($10^{19}/\text{cm}^3$). $\tau_M=4$ kg/mm^2 stressed for 200 sec. $T=500°\text{C}$.

For gallium doping the maximum variation in concentration between the top and bottom of the gauge length of the tensile specimens was less than a factor of 2. The variation was somewhat larger for crystals with arsenic impurity whose segregation coefficient in germanium is smaller than that of gallium. The details of the growth and perfection of these crystals have been published elsewhere.[3] Samples for the tensile experiments were cut from these crystals in the form described previously.[2] The deformation experiments were carried out at high temperature in an Instron machine. The method of Stein and Low[4] was used for the velocity measurements. The impurity concentrations were determined by Hall effect and resistivity measurements. In every instance specimens for Hall effect and resistivity measurements were cut from slices adjacent to the center of the guage length of the tensile bars. The accuracy of the resistivity and Hall effect measurements was within ±5%. The concentration of impurity carriers was calculated, assuming that the Hall coefficient $R_H=1/ne$ for n-type and $R_H=1/pe$ for p-type samples where e is the charge on the electron and n and p are, respectively, the electron and hole concentration.

RESULTS

Deformation Behavior of Heavily Doped Germanium

In order to compare the effects of impurities on the tensile deformation characteristics of germanium, it is essential that specimens of identical dislocation density be used. We have shown previously that dislocation-free intrinsic crystals of germanium deformed in tension in a hard machine show a large drop in stress at the yield point. The magnitude of the yield drop depends critically on the initial dislocation density.[2] In going from dislocation-free crystals to crystals with a dislocation density of $10^3/\text{cm}^2$, the maximum stress (σ_M) reached is decreased by about 40%. Hence, any small changes of σ_M due to impurities could easily be masked by the variation in the initial dislocation content of the samples. To eliminate ambiguity, *dislocation-free* crystals were used almost exclusively in these experiments. The tensile stress-strain curves of intrinsic and p- and n-doped germanium tested under identical conditions of temperature and strain rate are shown in Fig. 1. Both the doped and pure crystals exhibit the large yield drop associated with germanium crystals of high perfection. Doping with gallium raises the *maximum stress* σ_M at the *upper yield point* while arsenic lowers the *yield point*. The curve for the intrinsic crystal lies between that for the two doped crystals.

We have demonstrated that the occurrence of the yield point in intrinsic crystals of germanium[2] is not related to the static pinning of dislocations by impurity atoms. The yield behavior is to be understood rather on the basis of the dynamical behavior of dislocations in germanium. In the early stages of plastic flow few dislocations moving at a velocity determined by the applied stress contribute to plastic flow. The applied stress therefore increases until at σ_M enough dislocations are moving so that the rate at which the specimen deforms equals the deformation rate imposed by the machine. Beyond σ_M, dislocations continue to multiply and the stress drops until it reaches the flow stress. The experimental observations described below show that the yield drop in doped crystals is due to the same mechanism of the dynamical behavior referred to above.

As was observed for intrinsic germanium,[2] interrupted stress-strain experiments on gallium-doped germanium show that dislocations are first generated at stresses of the order of 25–30% of σ_M in the initial linear region of the stress-strain curve and depending on the pertaining experimental conditions may reach values between 10^5–$10^6/\text{cm}^2$ at the maximum stress. The effect of doping on the deformation behavior may be due either to its influence on the numbers generated as the specimen is deformed to σ_M or to its influence on the velocities of dislocations or to both. Information on the total numbers of dislocations generated can be obtained by interrupting the test at various elongations etching and counting the etch pit density. However, the number obtained in this way is the total number of dislocations present in the sample. The actual mobile numbers of dislocations which is the quantity of interest may be more or less than the total[5] depending on such factors as the temperature of test, the strain rate, the orientation of the sample, and the actual value of the stress at σ_M. Thus, the interpretation of any measurements of total numbers must be treated with caution. We have measured total densities in both doped and undoped crystals as a function of deformation and find them to be a factor of 2 higher in gallium-doped crystals over intrinsic crystals.

If dislocation multiplication and generation were solely responsible for the raising of σ_M with gallium doping, one would expect a smaller mobile number for

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[3] J. R. Patel, R. F. Tramposch, and A. R. Chaudhuri, *Metallurgy of Elemental and Compound Semiconductors* (Interscience Publishers, Inc., New York, 1961), p. 56.

[4] D. F. Stein and J. Low, J. Appl. Phys. 31, 362 (1960).

[5] A. R. Chaudhuri, J. R. Patel, and L. G. Rubin, J. Appl. Phys. 33, 2736 (1962).

the gallium-doped specimens as compared to intrinsic crystals. Since the total numbers measured are higher, it is unlikely that the numbers of mobile dislocations generated are smaller and hence responsible for the higher σ_M of gallium-doped crystals.

Dislocation Velocities in *p*- and *n*-Type Germanium

Average dislocation velocities were measured directly in doped germanium by the method of Stein and Low.[4] Similar measurements for intrinsic germanium have been described previously. The method consists of applying a nucleating center such as a scratch on a crystal surface and stressing in three-point bending so as to provide a variation of stress along the sample length. The load is applied for a given length of time and the velocities are computed from the distance the farthest dislocations have moved away from the scratch. Typical motion from a scratch as a nucleating center is shown in Fig. 2 for gallium-doped and arsenic-doped germanium.

The difference in dislocation velocity is illustrated quite strikingly in the photomicrographs comparing dislocation motion in gallium- and arsenic-doped crystals, Figs. 2(a) and 2(b). The results of such measurements of average velocity are shown plotted against resolved shear stress for doped and pure germanium in Fig. 3. For impurity concentrations of about $10^{19}/\text{cm}^3$, dislocation velocities are higher by a factor of 8 in arsenic-doped crystals over those in gallium-doped crystals. The stress dependence of dislocation velocity follows a relation of the form $v=v_0(\tau/\tau_0)^m$, where τ_0 is the stress necessary to drive a dislocation at a velocity v_0 of 1 cm/sec and v and τ are the velocity and applied shear stress, respectively. The exponent m for the doped crystals is about 1.5. The curve for intrinsic crystals lies between the arsenic and gallium curves.[5,6]

The velocity behavior in Fig. 3 is consistent with the deformation result in Fig. 1 and enables us to understand at least qualitatively why σ_M is greater than intrinsic for gallium and less than intrinsic for arsenic-doped crystals. Since the numbers generated are not too different, a lower dislocation velocity in gallium-doped crystals requires a higher stress at σ_M to generate the strain rate necessary to equal the applied deformation rate. Conversely, since dislocation velocities in arsenic-doped crystals are higher, the necessary strain rate at σ_M is achieved at a lower stress.

Quantitative estimates of the magnitude of the effect of doping on σ_M could be made if information on the numbers of mobile dislocations at any given amount of deformation was available. At σ_M, the mobile dislocation density can be calculated from the well-known relation ($\dot{\gamma}_p=Nbv$) where $\dot{\gamma}_p$ is the plastic shear-strain rate in the crystal, N is the mobile dislocation density, b is the burgers vector, and v is the dislocation velocity. At the maximum stress $\dot{\gamma}_p$ is known and equals the imposed machine strain rate which is $2Sc/L_0$, where Sc is the crosshead velocity and L_0 is the specimen gauge length. The values of N calculated from the measured velocities at σ_M (Figs 1 and 3) are $7.5\times10^5/\text{cm}^2$ for arsenic doping and $2\times10^6/\text{cm}^2$ for gallium doping. The over-all difference in the calculated mobile dislocation density for arsenic and gallium doping is less than a factor of 3 as compared to a factor of 8 for dislocation velocities. The calculations show that dislocation multiplication cannot be responsible for the effect of doping on σ_M since a higher σ_M for gallium doping would require a value of N lower than that for arsenic. Thus one must conclude that it is the effect of impurities on dislocation velocity that must be responsible for the observed variation of σ_M in Fig. 1.

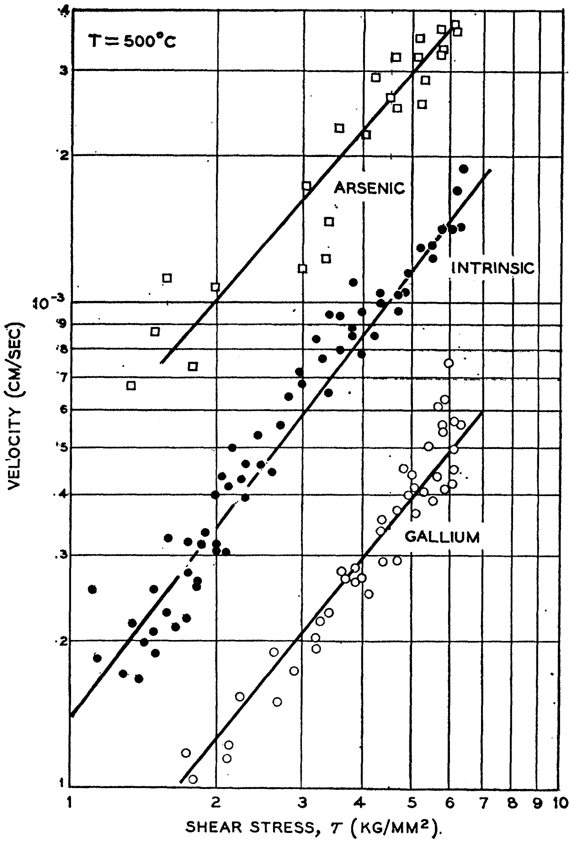

FIG. 3. Velocity of dislocations versus resolved shear stress. Arsenic doping ($10^{19}/\text{cm}^3$) raises dislocation velocity; gallium doping ($2\times10^{19}/\text{cm}^3$) lowers dislocation velocity compared to intrinsic. $T=500°\text{C}$.

Variation of Maximum Stress σ_M with Impurity Concentration

The effect of varying the concentration of gallium and arsenic impurities from $10^{13}/\text{cm}^3$ to about $10^{20}/\text{cm}^3$

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[6] Earlier measurements (Ref. 5) of dislocation velocity in undoped germanium at $T=500°\text{C}$ showed an exponent $m=1.9$ which was considerably higher than all the other exponents measured at various temperatures. Remeasured values of dislocation velocity shown in Fig. 3 show an exponent $m\approx1.4$.

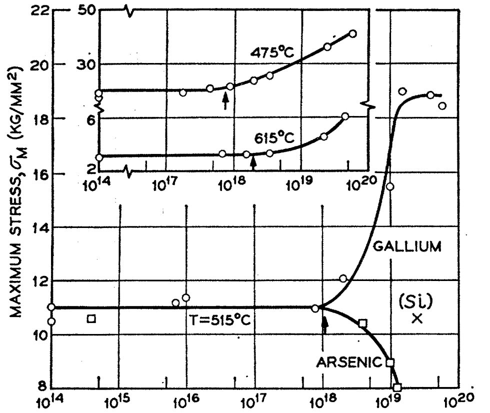

FIG. 4. Variation of σ_M with impurity concentration for arsenic and gallium impurity. Inset shows variation in σ_M for low and high temperatures. Arrows denote the intrinsic carrier concentration.

on the deformation behavior was investigated. In Fig. 4 the values of σ_M for crystals of different gallium and arsenic impurity concentrations are shown for a given crosshead velocity at a test temperature of 515°C. The value of σ_M is very nearly constant at about 11 kg/mm^2 over an extensive range of impurity concentrations (10^{13}–10^{18}/cm^3). At a concentration of about 10^{18}/cm^3, σ_M begins to increase for gallium doping and decrease for arsenic doping. As mentioned earlier dislocation-free crystals doped with gallium could be grown with relatively high-impurity concentrations. Hence values of σ_M could be obtained for impurity concentrations as high as 10^{20}/cm^3, whereas for arsenic the upper limit of concentration was about 10^{19}/cm^3. The value of σ_M for gallium doping is raised by almost a factor of 1.7. It may again be emphasized that a change of this magnitude could very readily be masked unless crystals free of dislocations are used.

The concentration where σ_M begins to change from its intrinsic value could be varied by changing the temperature of test. For instance lowering the temperature of test to 475°C lowered the concentration at which the break occurred to about 6×10^{17}/cm^3 (Fig. 4, inset), while increasing the test temperature to 615°C raised the concentration at which the break occurred. The critical concentrations for these two temperatures are shown in the inset, Fig. 4. For a given test temperature the concentration at which σ_M begins to increase or decrease appears to correspond approximately to the intrinsic carrier concentration at that temperature. The intrinsic concentrations are denoted by the arrows in Fig. 4.

Variation of Dislocation Velocity with Impurity Concentration

Since the effect of doping on σ_M is controlled primarily by the velocity of dislocations, the influence of impurities on dislocation velocities should exhibit behavior analogous to σ_M in Fig. 4. Velocity measurements at a fixed stress and temperature are shown in Fig. 5. The velocities for both gallium and arsenic doping appear constant up to a concentration of about 10^{18}/cm^3 at which point the velocities of the gallium-doped specimens decrease while the arsenic-doped specimens increase. The concentration at which σ_M changes for about the same test temperature is also approximately 10^{18}/cm^3.

Effect of Neutral Impurities

Neutral impurities (silicon and tin) have no effect on dislocation velocity or σ_M. At concentrations as high as 10^{19}–10^{20}/cm^3, both tin- and silicon-doped germanium crystals showed the same velocity and σ_M, respectively, as intrinsic crystals of germanium. Dislocation velocity for a tin doped crystal is shown in Fig. 5. The σ_M value for a silicon-doped crystal is shown in Fig. 4. The velocity behavior for crystals doped with neutral impurities is quite consistent with the corresponding behavior of the maximum stress σ_M.

Influence of Temperature on Velocity and σ_M at a Constant Impurity Concentration

The temperature dependence of both velocity and σ_M has been measured in heavily doped crystals with constant impurity concentration in the range of 10^{19}/cm^3. The temperature dependences of the dislocation velocities for arsenic- and gallium-doped crystals at a resolved shear stress $\tau=6$ kg/mm^2 are shown in Fig. 6. The temperature dependence of the dislocation velocity at a constant stress obeys a relationship[5] of the form $v=v_0(\tau)\exp(-E/kT)$, where $v_0(\tau)$ is a function of stress and E is the activation energy for the process. For intrinsic germanium, a plot of $\ln v$ versus $1/T$ gives a straight line with an activation energy of 1.57 eV which is independent of stress. For gallium doping, the activation energy is higher, about 1.75 eV, while doping with arsenic lowers the activation energy to 1.2 eV. For both impurities the magnitude of the change in velocity compared to intrinsic becomes larger the lower the temperatures, whereas the curves approach each other at high temperatures.

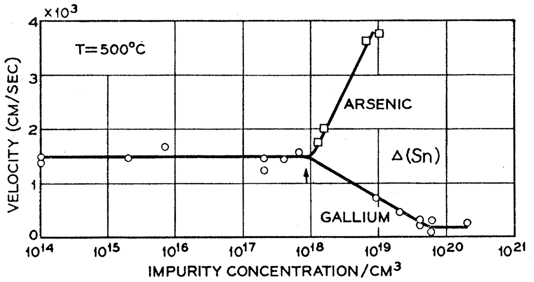

FIG. 5. Velocity versus impurity concentration at a constant shear stress $\tau=6$ kg/mm^2 for arsenic and gallium doping. $T=500$°C.

In intrinsic germanium we have shown that the pronounced temperature dependence of σ_M is due principally to the temperature dependence of dislocation velocity. Since at a given stress the difference in dislocation velocity between doped and pure crystals is higher the lower the temperature, one might expect a corresponding larger difference in σ_M at low temperatures. Compared in Fig. 7 are σ_M curves for intrinsic and gallium-doped crystals. At 400°C, σ_M for gallium-doped specimens is almost a factor of 2.5 greater than intrinsic, while at 700°C the difference is of the order of 20%.

DISCUSSION

The central question raised in this investigation is why the dislocation velocity is lowered with *p*-type and raised with *n*-type impurity with respect to undoped intrinsic crystals. No completely satisfactory mechanism which quantitatively answers this question is available at present. We can however consider some of the possible ways in which dislocation motion can be influenced in the diamond lattice and eliminate those whose predictions conflict with experiment.

Lattice Resistance

The remarkably straight polygonal forms assumed by dislocations upon plastically deforming germanium or silicon have been cited as strong evidence in favor of a high Peierls stress for the motion of dislocations in covalent crystals. The observations of regular geometrical forms have generally been made on crystals deformed at relatively low temperatures and for very slight deformations. At high temperatures and for large deformations, electron microscopy does not reveal very straight dislocations[7] or polygonal arrays. Nevertheless, in view of the strongly directional nature of the bonding, a large Peierls stress is expected in covalent crystals. In fact, calculations by Suzuki[8] on the energy of kink formation based on a calculation of Peierls force in covalent crystals gives an activation energy of 2.3 eV for silicon and 1.67 eV for germanium. This compares very favorably with our earlier finding[5] for the activation energy of dislocation velocity of 2.2 eV for silicon and 1.6 eV for germanium.

Haasen[9] has proposed that a crack of atomic dimensions is present at the core of a dislocation in the diamond lattice. When the dislocation moves the core must diffuse along with the dislocation. This is equivalent to the assumption of a high Peierls stress for dislocation motion. Based on this assumption the dislocation velocity in covalent crystals can be described

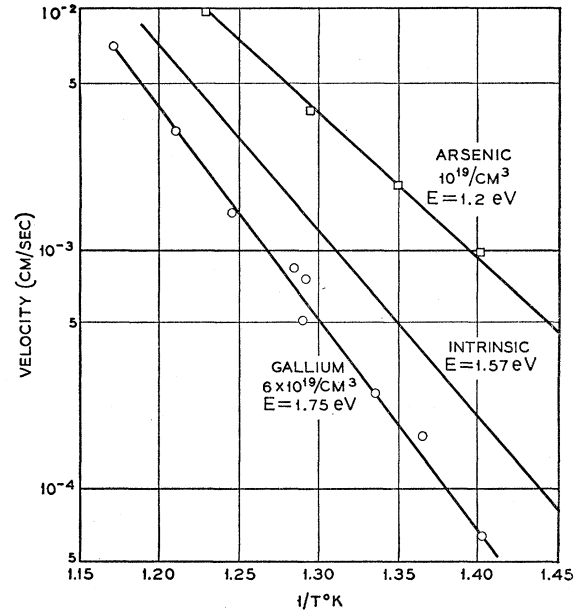

FIG. 6. Log velocity versus 1/T for arsenic- and gallium-doped crystals at a constant shear stress $\tau=6$ kg/mm². The activation energy is higher for gallium doping and lower for arsenic doping compared to intrinsic crystals.

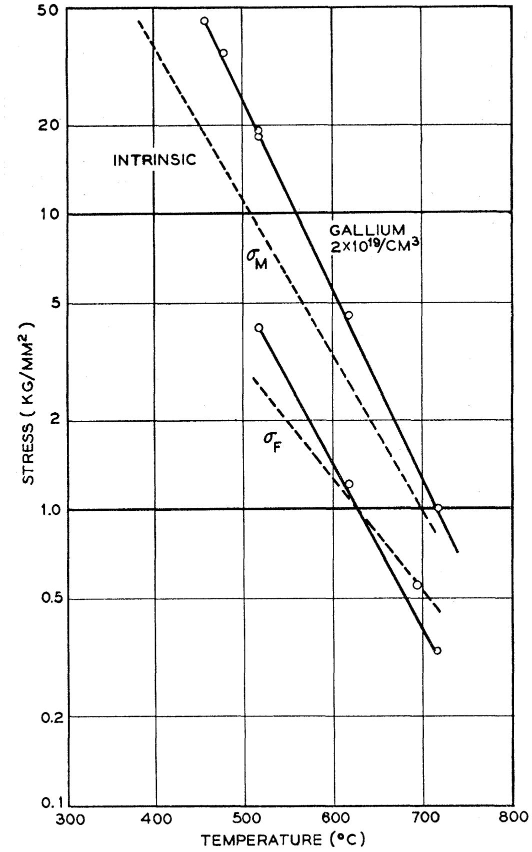

FIG. 7. Maximum and flow stress versus temperature for gallium-doped crystals compared to intrinsic crystals.

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[7] H. Alexander and S. Mader, Acta Met. **10**, 887 (1962).

[8] H. Suzuki, J. Phys. Soc. Japan **18**, Suppl. 1, 182 (1963).

[9] P. Haasen, Acta Met. **5**, 598 (1957). See also recent review in *Festkorperprobleme Band III* (Friedrich Vieweg und Sohn, Braunschweig, 1964).

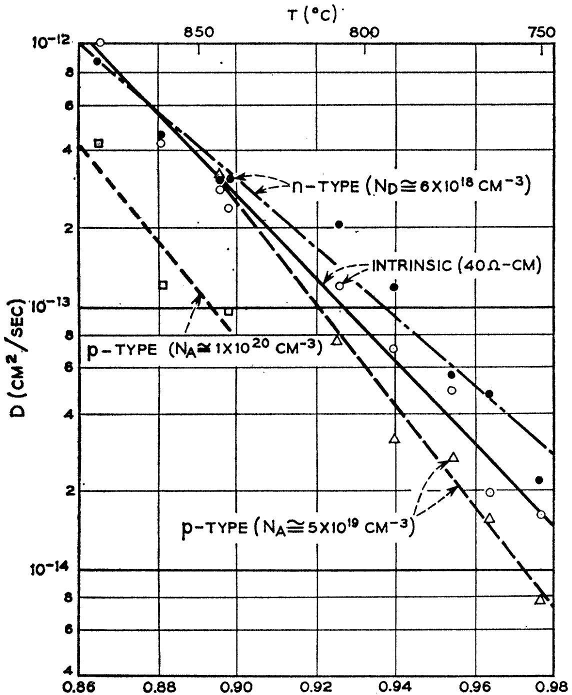

FIG. 8. Self-diffusion coefficient in arsenic- and gallium-doped germanium from Valenta and Ramasastry (Ref. 10).

by an equation of the form

$$v = (D_0 b^2 \tau / kT) \exp(-E/kT),$$

where $D = D_0 \exp(-E/kT)$ is the diffusion constant for the dislocation core. Experimentally[5] we have shown that except for a slight modification in the exponent of τ (from 1 to 1.5), the measured velocity of dislocations in germanium follow the above relation. To explain the effect of impurities we must assume that the diffusion constant D is changed. If we assume further that the diffusion of the dislocation core, requiring as it does the breaking and remaking of bonds, is in some way related to the self-diffusion of germanium, then there is a close analogy between the self-diffusion and velocity behavior in heavily doped germanium. Valenta and Ramasastry[10] have shown that doping heavily with *n*- or *p*-type impurities changes the self-diffusion coefficient of germanium. Doping with gallium lowers the diffusion coefficient while arsenic raises the diffusion coefficient. In Fig. 8 we reproduce from their paper the measured self-diffusion coefficients as a function of $1/T$. Note the similarity in behavior between the velocity vs $1/T$, in Fig. 6, and the diffusion data. The diffusion results are for temperatures higher than the velocity data; nonetheless, the general features are the same and the departures from intrinsic for both *n* and *p* type become greater at lower temperatures. Valenta and Ramasastry do not quote activation energies for their doped crystals; their curves, however, would indicate a higher activation energy ($\simeq 4$ eV) for *p* type and a lower activation for *n* type ($\simeq 2.6$ eV) as compared to intrinsic crystals (3 eV). Activation energies for self-diffusion behave roughly in the same way as the activation energies for dislocation motion in doped crystals.

The variation of self-diffusion coefficient with doping is explained on the basis of the common-ion effect in semiconductors. Since a vacancy acts as an acceptor in germanium we can write following Reiss and Fuller[11] the following equilibria for germanium doped heavily with a donor element such as arsenic

$$V \rightleftarrows V^- + e^+,$$

$$\begin{array}{l} \mathrm{As} \rightleftarrows \mathrm{As}^+ + e^- \\ \qquad\qquad\quad \uparrow\downarrow \\ \qquad\qquad\quad e^+e^-, \end{array}$$

where V is the vacancy and e^+e^- represents the hole-electron pair. If enough As is added, the vertical equilibrium will be forced down thus consuming more holes. The vacancy ionization equilibrium is shifted to the right, increasing the ionized vacancy concentration. Since the concentration of vacancies is constant at a given temperature and the total number of vancancies is $N_T = N_V + N_{V^-}$, the increase in ionized vacancy concentration N_{V^-} represents a real increase in the total concentration of vacancies. Similarly, doping with gallium decreases the concentration of vacancies. Of course, neither *p*- or *n*-type impurities exert any effect on the vacancy concentration until their concentration exceeds the intrinsic concentration of electrons or holes. For our experiments the effect of doping on dislocation velocity or σ_M, Figs. 4 and 5, is not observed until the intrinsic carrier concentration is reached.

Thus Haasen's model of a viscous diffusion-like motion of the dislocation core in germanium,[9] in conjunction with the effects of acceptor and donor impurities on self-diffusion in germanium[10] and the common-ion effect as applied to vacancies and donors in germanium,[11] is, at least qualitatively, consistent with the effects of donor and acceptor impurities on dislocation mobility in germanium.

For undoped germanium the main argument in favor of Haasen's theory is that it very nearly approximates the correct stress and temperature dependence of dislocation velocity in covalent crystals. It appears plausible to extend the theory to the observations on heavily doped crystals although here the arguments are much more tenuous and qualitative. The detailed microscopic behavior of the dislocation core cannot be treated by the theory and the activation energy for dislocation motion must be determined from experiments. This is an unsatisfactory feature since it cannot permit an insight into the mechanism by which dislocation velocities are retarded or speeded up by impurities.

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[10] M. W. Valenta and C. Ramasastry, Phys. Rev. **106**, 73 (1957).

[11] H. Reiss and C. Fuller, *Semiconductors*, edited by N. B. Hannay (Rheinhold Publishing Corporation, New York, 1959), p. 243.

Drag Due to Jogs

Jogs on screw dislocations can act as a brake on dislocation motion. Dash[12] has shown that the motion of screws in silicon can be restricted by the formation of defect trails left in its wake. Curvature of the dislocation line in the region of the defects indicates that dislocation mobility is at least locally restricted. Seitz[13] has pointed out that the static frictional force or Peierls stress should be larger for jogs than for dislocation lines lying in close packed planes. According to Friedel[14] this is especially so in crystals such as silicon or germanium where the Peierls stress is already high for a glide dislocation. If a jog moves nonconservatively and creates defects, the stress required is proportional to the formation energy of defects.[13] In order to account for the velocity behavior in *p*- and *n*-doped germanium one must postulate (since dislocations move faster in *n*-type germanium) that defects are formed more easily in heavily doped *n*-type crystals and with greater difficulty in *p*-type crystals, than in intrinsic crystals. According to Longini and Greene,[15] heavy doping changes the ionized vacancy concentration by modifying the activation energy term in the expression for the ionized vacancy concentration by an amount corresponding to the shift in the Fermi level from its intrinsic value. It was assumed (as in the previous section) that the increase or decrease, in the vacancy concentration with impurities, was produced under equilibrium conditions. For our conditions of deformation, defect production by dislocation motion is not an equilibrium process. Furthermore, one must postulate that dislocation motion in intrinsic crystals is also controlled by jogs. We have previously shown[5] that because of the negligible stress dependence of the activation energy for dislocation velocity, the spacing of jogs can at most be a few Burgers vectors which is orders of magnitude less than the spacing observed by Dash. In the absence of a suitable mechanism for their origin, the presence of such a high density of jogs is highly questionable. While some sort of dislocation vacancy interaction with jogs cannot be entirely ruled out, the above arguments suggest that drag due to jogs is probably not the dominant factor influencing dislocation velocities in doped crystals.

Interaction with Vacancies

As discussed above the equilibrium concentration of vacancies in heavily doped crystals depends on the type of doping being higher in *n*-type crystals and lower in *p*-type crystals. During dislocation motion the strain field of a dislocation should interact with the strain field of a vacancy thus influencing dislocation mobility. On the basis of this argument one would expect a lower dislocation velocity for dislocations in *n*-type germanium because of the larger concentration of defects with which the dislocation has to interact, and a higher dislocation velocity for *p*-type germanium because of the lower vacancy concentration. Experimentally, exactly the opposite is true, and thus a vacancy-dislocation interaction mechanism may be ruled out.

Pinning Due to Impurities

In both doped and undoped[2] crystals of germanium numerous strain-aging experiments have failed to show that the yield point is due to pinning of dislocations by impurities. In any case the tetrahedral covalent radii[16] of both arsenic and gallium are nearly the same as that of germanium, thus the interaction due to the strain field of the impurity with dislocations is not expected to be widely different for *p* and *n* dopings. Furthermore, high concentrations of neutral impurities such as tin or silicon do not influence dislocation velocities at all, so that pinning effects cannot be responsible for the observed doping effects. Cummerow and Cherry[17] have reported a pinning effect in germanium doped with $\sim 2\times 10^{19}/\mathrm{cm}^3$ arsenic. Specifically their findings show that when lightly bent samples of germanium doped heavily with arsenic or gallium impurities are annealed, thermally induced glide into the neutral axis of the bar is observed in gallium-doped crystals but not in arsenic-doped crystals. They attribute this to the pinning of dangling bonds with the available 5th valence state in arsenic. On this basis pinning should result in a lower dislocation velocity for arsenic doped crystals and a higher velocity for *p*-type crystals, while all of our experiments are consistent with a higher dislocation velocity in *n* doped crystals than in *p*-type crystals. We are unable at present to reconcile the reported pinning experiments with our results. Certainly in our strain aging experiments enough impurities are present to saturate all the dislocations generated beyond the yield point. It is highly unlikely that a recovery of the yield point would not be observed if pinning due to arsenic impurity does occur.

Charged Dislocations

It has been reported that dislocations in germanium act as acceptors with a level[18] 0.2 eV below the conduction band. Let us for the sake of argument accept the above value. Then for *n*-type germanium the dislocation levels are not occupied for high temperatures and moderate dopings, since the Fermi level is

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[12] W. C. Dash, J. Appl. Phys. **29**, 705 (1958).

[13] F. Seitz, Advan. Phys. **1**, 43 (1952).

[14] J. Friedel, *Dislocations* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1964), p. 120.

[15] R. L. Longini and R. F. Greene, Phys. Rev. **102**, 992 (1956).

[16] W. C. Dunlap, Jr., Phys. Rev. **94**, 1531 (1954).

[17] R. L. Cummerow and A. R. Cherry, Phys. Letters **3**, 367 (1959).

[18] Recently R. M. Broudy, Advan. Phys. **12**, 135 (1963), reports an acceptor level 0.5 eV below the conduction band. The way in which the acceptor level varies with temperature is not known. In the temperature range of our investigation the energy gap of germanium is about 0.4 eV as compared to 0.66 eV at room temperature.

approximately at the center of the energy gap. With the addition of large amounts of *n*-type impurities the Fermi level moves towards the conduction band and the acceptor levels begin to fill until we reach a point where the Fermi level is above the dislocation acceptor level and all the acceptor sites are occupied. Read[19] has calculated the statistics of the occupation of acceptor sites for dislocations at low temperatures and finds that at 0°K with the Fermi level well above the dislocation acceptor level about 0.1 of the sites are occupied. Thus in *n* type germanium we expect the dislocation to be negatively charged with, as Read has shown, a *p*-type space-charge cylinder surrounding the charged dislocation. On the other hand, in undoped and heavily doped *p*-type germanium, the acceptor levels are substantially unoccupied since the Fermi level is always below the acceptor level, assuming that the dislocation acceptor level still lies in the upper half of the energy gap at high temperatures. If the observed doping effects on dislocation velocity are to be ascribed to charged dislocations, one would not expect the behavior of intrinsic and of heavily doped *p*-type crystals to be greatly different. Our results clearly show that a *p*-type impurity lowers dislocation velocity by as much as *n* type increases it over the intrinsic value. If the level due to dislocations is at the center of the gap one could expect differences in the occupation of dislocation acceptor levels with the addition of *p*- or *n*-type impurities. In view of the uncertainty in the position of the dislocation level and its variation with temperature, one cannot say with certainty what the charge on a dislocation and consequently its effect on dislocation velocity is likely to be in heavily doped crystals.

CHARGED IMPURITIES IN SILICON

There is no clear evidence on the electrical effects of either vacancies or dislocations in silicon. We have attempted to observe effects similar to those in germanium in silicon crystals heavily doped with boron or arsenic in the range $10^{19}/\text{cm}^3$. Unfortunately, at these heavy doping levels it is not possible to etch dislocations readily in silicon. Thus we could not compare dislocation velocities in doped silicon with values measured in undoped crystals. Deformation measurements at 800°C on both arsenic- and boron-doped crystals showed that σ_M was unchanged from the undoped value. At 800°C for silicon the intrinsic carrier concentration is about $10^{18}/\text{cm}^3$, thus an effect should have been seen at doping levels of $10^{19}/\text{cm}^3$. We tentatively conclude that doping heavily with acceptor or donor impurities in silicon does not affect the deformation behavior in silicon.

SUMMARY

(1) Electrically active impurities can exert a large effect on the deformation behavior of germanium. Specifically, a *p*-type impurity (gallium) raises the maximum stress while an *n*-type impurity (arsenic) lowers the maximum stress compared to that of intrinsic crystals.

(2) The effect of impurities on the deformation behavior is a necessary consequence of the fact that the velocity of dislocations is lower in gallium-doped germanium and higher in arsenic-doped germanium compared to velocities in intrinsic germanium.

(3) The effect of impurities on dislocation velocity is not noticeable until the impurity concentration in the crystal reaches the intrinsic carrier concentration for the relevant test temperature.

(4) For a constant impurity concentration in the range of $10^{19}/\text{cm}^3$, the magnitude of the effects on σ_M and velocity are higher at lower temperatures.

(5) For a given stress, dislocation velocity depends exponentially on temperature with activation energies of 1.57 eV for intrinsic crystals, 1.75 eV for crystals with $2\times10^{19}/\text{cm}^3$ gallium, and 1.2 eV for specimens with $10^{19}/\text{cm}^3$ arsenic.

(6) Neutral impurities, tin and silicon, do not appear to affect either σ_M on velocity at concentrations as high as $10^{19}/\text{cm}^3$.

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[19] W. T. Read, Phil. Mag. 45, 115 (1955).

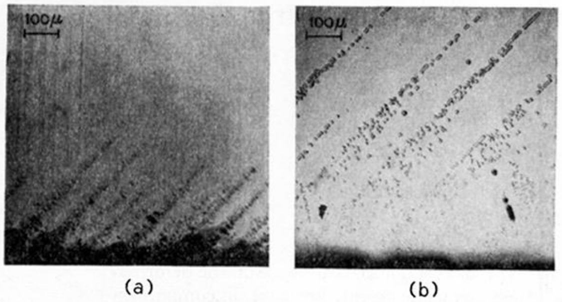

FIG. 2. Dislocation motion from a scratch. (a) Gallium ($2\times10^{19}/\text{cm}^3$). $\tau_M=4$ kg/mm^2 stressed for 50 sec. (b) Arsenic ($10^{19}/\text{cm}^3$). $\tau_M=4$ kg/mm^2 stressed for 200 sec. $T=500°\text{C}$.