DISLOCATIONS IN SEMICONDUCTOR CRYSTALS

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Usp. Fiz. Nauk 72, 479-494 (November, 1960)

INTRODUCTION

BECAUSE of the widespread introduction of semiconductors into technology, much attention is currently being given to growing semiconductor single crystals having an almost perfect crystalline structure, i.e., almost without defects.

Dislocations are among the most important of crystal lattice defects. Dislocations in crystals have been the subject of theoretical work since 1930. More recently their existence has been confirmed experimentally.[1-4]

The theory of dislocations has been considered in detail by Read,[5] Cottrell,[6] and I. Oding.[7] Indenbom[8] has discussed the most important work on dislocations by Soviet and foreign authors up to 1958. Dislocations in germanium single crystals have been reviewed in reference 9. V. Regel', A. Urusovskaya, and V. Kolomiĭchuk[10] have discussed the problem of revealing dislocations in crystals by etching. In the present review we consider dislocations in semiconductor crystals. Attention is centered on the effect of dislocations on the electrical properties of semiconductor crystals, the methods of revealing dislocations in them, the way dislocations arise in the growth process, and their effect on the properties of semiconductor devices.

At the present time dislocations have been adequately studied in germanium and silicon crystals. They have been studied less in other semiconducting materials. Dash,[11] by studying the reasons why dislocations arise in silicon single crystals, has found a method of growing dislocation-free single crystals of silicon and germanium.

THE EFFECT OF DISLOCATIONS ON THE ELECTRICAL PROPERTIES OF SEMICONDUCTORS

Around a dislocation the crystalline lattice is distorted: in some places it is compressed, in others extended. The degree of lattice distortion depends on the dislocation type. Usually only edge and screw dislocations are considered. But, as Hornstra[12] showed, in the diamond lattice, which silicon and germanium have, other types of dislocation are also possible — in particular, simple 60° dislocations. Lattice extensions and compressions change the positions of the upper edge of the valence band E_V and the lower edge of the conduction band E_C. As Shockley and Bardeen[13] showed, the change of position of the bands can be expressed as follows:

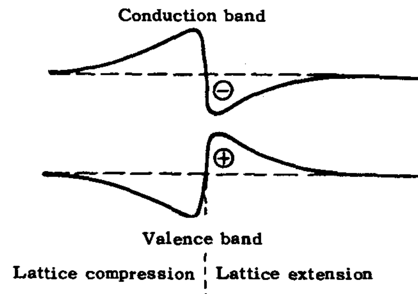

FIG. 1. The change of the forbidden gap width around a positive edge dislocation.

$$E_c = E_{c0} + \varepsilon_c \frac{\Delta V}{V}, \quad (1)$$

$$E_v = E_{v0} + \varepsilon_v \frac{\Delta V}{V}, \quad (2)$$

where $\epsilon_C = \partial E_C/\partial V$, $\epsilon_V = \partial E_V/\partial V$, E_{C0} is the position of the conduction band edge in the perfect semiconductor and E_{V0} the position of the valence band edge in the perfect semiconductor, and ΔV is the volume change of the crystal.

The change in the width of the forbidden gap can be expressed as

$$\Delta E = (\varepsilon_c + \varepsilon_0) \frac{\Delta V}{V}. \quad (3)$$

In Fig. 1 is shown the change in the forbidden gap width around a positive edge dislocation. In the region of lattice extension the width of the forbidden gap is decreased and in the region of compression increased. Since electrons usually have a tendency to find themselves in levels with minimum energy, i.e., in the lowest states of the conduction band, and the holes in the highest states of the valence band, the greatest probability of their normal recombination will be found in the region of lattice extension.

Hornstra[12] showed that in the diamond-type lattice atoms of germanium or silicon at 60° and edge dislocations have a row of unsatisfied tetrahedral bonds, with one or two unpaired electrons. Such unpaired bonds have been called "dangling" by Shockley. The theory of the unpaired bond with one electron as an acceptor center of the dislocation line has been developed by Read.[16-18]

For brevity, 60° and edge dislocations will be called simply dislocations. Screw dislocations do not usually give unpaired bonds; therefore they have a negligible effect on the electrical properties of crystals; for this reason only the effect of edge and 60° dislocations will be considered in what follows.

According to Read's theory the atoms with unpaired bonds along the dislocation line are able to capture free electrons from the conduction band to complete tetrahedral bonds. After an electron has been captured by the acceptor level of the dislocation, its energy is greater than that of an electron in the valence band but smaller that that of an electron in the conduction band. We will assume that in n-type germanium, if dislocations are suddenly created, for example by deformation, the acceptor centers along the dislocation line will be filled by electrons from the conduction band. As a result the dislocation becomes a negatively charged line. To neutralize this charge, a positive space charge forms in the vicinity of the dislocation. Since the acceptor centers are situated at the dislocation along a single line, when they are filled by electrons they repel other electrons and a proportion of the centers therefore remains unfilled. The degree of filling of the dislocation acceptor levels can be expressed by the function

$$f = \frac{1}{1 + e^{\frac{E_d - E_F}{kT}}}, \tag{4}$$

where k is the Boltzmann's constant, T is the absolute temperature, E_F is the position of the Fermi level, and E_d is the position of the acceptor level of the dislocation. The formation of space charge in the semiconductor around dislocations increases the scattering of carriers and decreases their mobility.

The investigations of Gallagher[19] and Pearson[20] have shown that dislocations arising in germanium as a result of plastic deformation create acceptor levels in the forbidden gap 0.2 ev below the conduction band. It has been established in a number of cases that plastic deformation causes a sharp change in the specific resistance and even the conversion of germanium from n-type to p-type.[21–25]

The introduction of dislocations into semiconducting crystals increases the recombination of charge carriers. The mechanism of recombination at dislocations is different in n-type and p-type semiconductors. Wertheim and Pearson[26] have explained the mechanism of recombination of charge carriers in plastically deformed germanium as follows. For p-type material the recombination of charge carriers includes the direct capture of the excess electron from the conduction band by the neutral dislocation center and the subsequent recombination with a hole in the valence band.

At low temperatures all the acceptor centers of the dislocations are in the neutral state, and the temperature variation of the lifetime reflects the change of the capture radius r according to the following empirical formula:

$$r = 3.4 \cdot 10^{-8} (300/T)^3. \tag{5}$$

The lifetime at room temperature in deformed p-type germanium is given by:

$$\tau = 0.7 \cdot N_d^{-1}, \tag{6}$$

where N_d is the density of dislocations.

In n-type germanium the process of recombination includes the capture of the surplus hole by the negatively charged dislocation center, which is thus transformed into a neutral state, and the subsequent capture of an electron from the conduction band. The lifetime of minority carriers is given at room temperature by the relationship:

$$\tau = 2.5 N_d^{-1}. \tag{7}$$

McKelvey[27] has investigated the recombination of carriers in germanium and found that the recombination cross section of dislocations is in the form of a cylindrical region, with diameter 1.15×10^{-8} cm for holes in n-type germanium, and 2.8×10^{-8} cm for electrons in p-type germanium.

In n-type germanium at low temperatures a delayed decay of photoconductivity is observed. Morrison[28] explains this phenomenon as due to the existence of space charge at the dislocations.

The results of experimental investigations on carrier recombination at dislocations can be divided into two groups. The results in the first group refer to the effect on recombination in semiconductor crystals of those dislocations which arise in the growth process. In what follows we will call these "grown-in" dislocations. In their behavior they differ to some extent from dislocations which arise during plastic deformation. All the remaining results belong to the other group.

The study of the recombination properties of "grown-in" dislocations in germanium has been the subject of references 29 to 33.

Data on carrier recombination in germanium obtained by various authors is presented in Fig. 2. As is seen from the figure, "grown-in" dislocations affect the recombination velocity less than dislocations arising during plastic deformation.

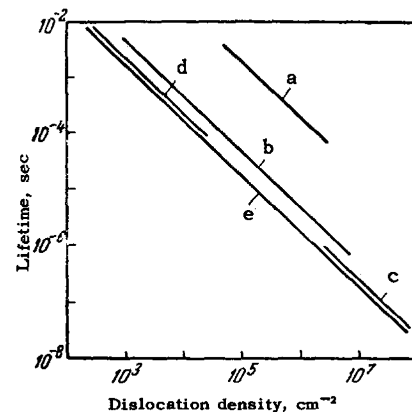

FIG. 2. Variation of minority carrier lifetime in germanium with dislocation density at room temperature: according to the data of a) Kulin and co-workers,[31] b) Kalvey,[27] c) Wertheim and Pearson,[26] d) Okada,[33] e) Hasiquti and Matsuara.[32]

TABLE I

σ	Specific resistance	Conductivity type	Type of dislocation	Ref.
$5.5 \cdot 10^{-4}$	30	n	Grown-in	31
$3.5 \cdot 10^{-3}$	3.5	n	»	31
$5.8 \cdot 10^{-1}$	2.5	n	»	33
$6.0 \cdot 10^{-1}$	3–7	n	»	32
$3.6 \cdot 10^{-1}$	8	n	Deformation	26
1.43	2.2	p	»	26

If it is assumed that each dislocation acts as a recombination center, the recombination velocity in an n-type semiconductor can be expressed by the formula

$$\frac{\Delta p}{\tau} = \sigma N_d \Delta p, \tag{8}$$

where τ is the hole lifetime, σ is the capture cross section, N_d is the dislocation density, Δp is the excess concentration of holes, and

$$\sigma = 1/\tau N_d. \tag{9}$$

The values for σ obtained by various authors are given in Table I both for "grown-in" dislocations and for dislocations arising during plastic deformation of germanium single crystals. The different effect of "grown-in" dislocations and dislocations formed during deformation can be explained by assuming that dislocations arising in the growth process of the crystal have an impurity atmosphere, while dislocations arising during plastic deformation have no impurity atmosphere.[34] A rigid correlation between the density of "grown-in" dislocations and the lifetime of minority carriers is not observed. Nor is there a unique result for the capture cross section of the dislocations. This apparently indicates that the impurity atmosphere at the dislocations is thicker in some cases than in others. In addition, the recombination velocity is affected by the type of impurities that make up this atmosphere.

THE INTERACTION OF DISLOCATIONS WITH IMPURITY ATOMS

The stress field around a dislocation can interact with other sources of internal stress in the lattice. It can attract to itself impurity atoms and decrease the general stress in the crystal.

Cottrell[6] showed that the energy of interaction of an edge dislocation with an impurity atom can be written approximately in the following form:

$$U = \frac{4}{3}\frac{1+\nu}{1-\nu}\frac{\mu b \varepsilon r_A^3 \sin\alpha}{R}, \tag{10}$$

shear ν is Poisson's ratio, μ is the shear modulus, b is the Burgers vector, $\epsilon = (r_1 - r_A)/r_A$, r_A is the atomic radius of the solvent, r_1 is the atomic radius of the impurity, α and R are the polar coordinates of the impurity atom relative to the position of the edge dislocation.

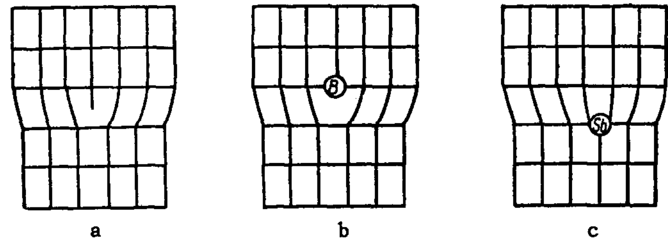

FIG. 3. The possible disposition of impurity atoms around an edge dislocation: a) dislocation free of impurity, b) dislocation having an impurity atmosphere of atoms, the radius of which is smaller than the solvent atom radius, c) dislocation with an impurity atmosphere of atoms whose radius is greater than the solvent atom radius.

Impurity atoms whose radius is greater than the radius of the solvent atom will be attracted to the lower part of a positive edge dislocation, whereas impurities whose atomic radius is smaller will be attracted to the upper part.

In Fig. 3 are shown the possible dispositions of impurity atoms around an edge dislocation. In case a) the dislocation is free of an impurity atmosphere. The impurity atmosphere around the dislocation is formed by atoms of boron in case b) and by atoms of antimony in case c).

In Table II are given the values of the interaction energy of several impurity atoms with edge dislocations in germanium and silicon; the values apply when the impurity atom is at a distance of 4 A from the dislocation line.[14]

The equilibrium distance of an impurity atmosphere from a dislocation can be expressed, using the law of mass action as:[34]

$$f = \frac{1}{1 + A/N \cdot \exp(-U/kT)}, \tag{11}$$

where f is the fraction of sites occupied by impurity atoms, N is the concentration of impurity atoms, which is assumed far greater than that of the unsaturated bonds at the dislocation, U is the energy of the bonding of the impurity atoms at the dislocation. The equation holds[9] if U does not depend on f, but this condition is not satisfied for moderately high impurity concentrations.

For germanium heavily doped with antimony or boron the impurity atmosphere will be held at the dislocations up to temperatures close to the melting point.[34]

TABLE II

Impurity	Atomic radius	ε	U, ev
Cu	1.28	0.0492	0.12
As	1.66	0.0492	0.12
Al	1.43	0.1720	0.36
Sb	1.34	0.0983	0.20
Sn	1.45	0.1880	0.48
P	0.93	0.2370	0.54
Si	1.18	0.0328	0.06

TABLE III

No.	Material studied	Conventional name of reagent	Reagent composition	Time and conditions of etching	Ref.
1	Germanium	CP-4	50 cc HNO_3 68% +30 cc CH_3COOH 99.8% +30 cc HF 48% + 0.6 mg Br		2
2		Alkali	12 g KOH + 8 g $K_3[Fe(CN)_6]$ + 100 cc H_2O	2-6 min in boiling solution.	40
3		№ 1	2 cc HNO_3 + 4 cc HF + 40 cc H_2O +200 mg $Cu(NO_3)_2$	6-7 min in cold etch.	36
4		№ 2	10 cc H_2O_2 30% +10 cc HF 48% + 40 cc H_2O	3-6 min in cold etch.	45
5		Iodine	20 cc HNO_3 + 16 cc HF + 8 cc CH_3COOH + 0.3 mg I	up to 15 min in cold etch.	41
6	Silicon	CP-4	10 parts HF 48% +10 parts HNO_3+Conc +20 — 50 parts ice + 1 part Br		46
7					47
8			1 part HF + 3 parts HNO_3 +10 parts CH_3COOH glacial	4—24 hr	3
9			4 parts HF 48% + 5 parts HNO_3 75% + 2 parts CH_3COOH glacial + 1 part 1/32 molar KNO_3 solution		48
10			1 part H + 3 parts HNO_3 +15 parts CH_3COOH		44 49
11	Silicon-germanium alloys	CP-4	1 part HF + 1 part HNO_3		50
12	In Sb		10 parts HNO_3+ 40 parts lactic acid	2—5 sec	51
13			C_2H_5COOH+5 parts HF+15 parts H_2O		

Impurity atmospheres reduce the effectiveness of dislocations as recombination centers. As the temperature increases the impurity atoms can overcome the potential barrier U of the dislocation, and move throughout the crystal. The probability of an impurity atom breaking away from the dislocation is proportional to $\exp(-U/kT)$.

If $kT \gg U$, the impurity atoms can distribute themselves randomly throughout the entire crystal. When the dislocations are freed from the impurity atmosphere, unsaturated bonds appear, which, to complete paired covalent bonds, can capture free electrons from the conduction band and thus decrease the lifetime of minority carriers. The formation of an impurity atmosphere around a dislocation decreases the effective capture cross section for carriers.

Upon sufficiently rapid cooling from high temperatures to lower temperatures impurity atoms are locked in a crystal in a random distribution. Because of their low mobility at low temperatures they cannot again form an impurity atmosphere around a dislocation. On the other hand, slow cooling of specimens from high temperatures makes the formation of such impurity atmospheres possible. In this way the increase and decrease of lifetime in germanium specimens during heat treatment can be explained to some extent.

Impurity atoms make the motion of dislocations more difficult. During the motion of dislocations, vacancies can be formed very easily. If all the portions of a dislocation do not lie in the glide plane, then each non-gliding part on the dislocation line leaves behind, during forced motion, a train of vacancies and atoms in interstices. Moving dislocations, on crossing other dislocations, leave behind, during their further motion, a planar region of point defects which then gradually dissolve in the crystal.[35]

THE DISPLAY OF DISLOCATIONS

Several methods exist for displaying dislocations in crystals. We shall dwell briefly on only some of them.

The metallographic method. Recently the metallographic method of revealing dislocations has found wide applicability not only for semiconductors but for other crystals also. In reference 10 the results of displaying dislocations by this method are reviewed concisely. In the present section we will deal only with those questions which were not adequately treated in that review.

The metallographic method of revealing dislocations is based on the fact that the rate of solution of the crystal surface by an etch is greater in places where the crystal lattice is distorted than where it is undistorted.

It has been established that the places where dislocations intersect the surface of the crystal are more easily attacked by various solvents.[2] This is associated with the fact that the atomic bonds are distorted around the dislocation lines in the crystal: at some places they are extended, in others compressed, or even broken. The region of crystal around the dislocation has an additional energy. This makes the places where dislocations emerge to the surface less resistant to the effect of chemical etches. Because of the differ-

ent rates of etching on the surface of the crystal, characteristic etch pits are formed at the places where dislocations come out. Their form depends on the crystallographic orientation of the surface under consideration, the structure of the lattice, the composition of the etch used, and the inclination of the dislocation line to the surface of the crystal.[36-38] Usually, in order to display more accurately the general density of dislocations as well as the internal structure of the etch pits themselves, etching reagents are used which dissolve the crystal surface slowly.

Table III lists the compositions of the reagents most widely used to display the dislocation densities in various semiconductor crystals.

Etch pits on the surface of germanium where dislocation lines emerge are usually displayed on the {111} and {100} planes. On a {110} surface, because of the small difference in the etching rate, pits either do not generally form or form very weakly and are very difficult to distinguish under the microscope.

The reagent CP-4 (see Table 3, No. 1) is widely used to display dislocations in germanium. The etch pits formed by CP-4 on the {111} plane frequently have the form of right cones. The angle at their vertex is usually 166°.

Pfann and Vogel[3] found no noticeable difference in the form and dimensions of etch pits on n- and p-type germanium, and on pure and impure germanium (containing in the latter case 0.01% of elements of Groups III and V). They surmise that an impurity atmosphere has no effect on the formation of pits.

Dislocation etch pits appear on surfaces that depart by not more than $8-10°$ from the {100} or {111} planes. In the authors' opinion the slope of the dislocation line plays no part. If the plane of observation departs from the {100} or {111} planes, the pits have an elliptical or U-shaped form. The form of the pits depends basically on the method of etching.

Billig,[40] after preliminary experiments on the determination of the dislocation density by the metallographic method using a series of reagents, including CP-4, found that an alkali gave the best results. The etch pits it produces on a {111} surface have the form of equilateral triangular pyramids. When the plane under study departs from {111}, the edges of the pit form elongated triangles, and their vertex is displaced towards the side.

Ellis[36,37] used reagent No. 2, which, unlike CP-4, reveals structure in the walls of the pit, for investigating dislocations in germanium single crystals. This reagent typically produces a central hollow surrounded by a large number of irregular terraces. Ellis proposes that the terraces show bends or steps in the dislocations which, when they are reached, diminish the effect of the reagent perpendicular to the surface. If reagent No. 2 is diluted with an equal amount of water, then pits appear with spiral terraces.

Rhodes[41] used a modified CP-4 composition in which crystalline iodine was used instead of bromine. When single crystals of germanium are etched in this reagent, pits of large and small dimensions are formed. The pits of small dimensions have spiral-like terraces. The density of these pits is approximately one or two orders of magnitude greater than the density of pits displayed by DP-4. Usually these pits also occur in different places. The authors propose that they are formed where screw dislocations intersect the surface of the crystal.

In contradistinction to germanium, etch pits in silicon form on any crystallographic surface.[42,43] The form of the etch pits depends on the crystallographic orientation of the plane studied. Johnston[44] observed etch pits with spiral terraces on {110} and {111} surfaces after etching in a solution consisting of 15 parts acetic, 3 parts nitric and 1 part hydrofluoric acid. Besides these pits, he also observed pits of larger dimensions which, in his opinion, were associated with edge dislocations.

The principal inadequacy of the metallographic method is that it does not allow one to obtain an idea of the distribution of dislocations in the volume of the crystal. The determination of the dislocation density by this method is greatly hampered if the density exceeds 1×10^5 cm^{-2}. In this case the closely placed dislocations can be confused with one another under the microscope. Also, not every pit can be taken to be the place where a dislocation line emerges to the surface. Because of the small difference in the etching rates where screw dislocations come out and in perfect parts of the grain, not all screw dislocations can be revealed. In order to obtain a sufficiently correct picture of their distribution, it is necessary to choose a reagent with sufficiently small solution rate. Apart from this, dislocation lines coming out to the surface inclined at more than 30° to the normal do not give pits at all.

Despite the inadequacies mentioned above, the metallographic method finds wide use, since it is very simple, does not require complicated apparatus, and enables the properties of various surfaces to be characterized. It can be successfully used to display dislocations in studies of the growth of perfect semiconductor crystals.

The x-ray method. This method differs from the metallographic one in that the specimen itself is not destroyed when the dislocation density is being determined.

The x-ray beam reflected from an ideal crystal is narrow. The presence of dislocations creates disorientated regions which broaden the diffraction curve. Kulin, Kurtz and Averbach[31] used a two-crystal method to determine the density of dislocations in germanium. In order to isolate the effect of the plastic broadening, two crystals were used. In one position was a perfect single crystal, in the other the specimen to be studied.

Under the assumption that the dislocations are distributed uniformly throughout the crystal, the density of dislocations N_d as a function of the angle of broadening of the diffraction curve is given by

$$N_d = k^2/9b, \tag{12}$$

where $k = (\beta^2 - \Phi^2)^{1/2}$, k is half the effective width of the curve in seconds, Φ is half the width of the curve given by the control crystal, β is half of the measured width of the curve, and b is the Burgers vector.

The x-ray method gives a more accurate impression of the density of dislocations in the crystal and allows specimens to be prepared for study while preserving the original distribution of the dislocations.

The metallographic method, as the investigations of Kulin et al.[31] showed, agrees quite well with the results obtained by the x-ray method if the dislocation density is less than 1×10^6 cm^{-2}.

A comparison of the results of determining the dislocation density by the metallographic and x-ray methods is given in Fig. 4. When studying the distribution of the dislocation density, both methods complement one another.

More recently other variants of the x-ray method have appeared. To determine the density of dislocations, Lang[52] passed a plane beam of x rays through a crystal of silicon so that the reflected beam was perpendicular to the crystal surface. By studying the distribution of intensity of the reflected beam, which was recorded on a photographic plate, he obtained quite accurate data on the distribution of dislocations in the volume of the crystal.

References 33 — 54 also describe x-ray methods of studying dislocations in crystals.

The decoration method. For studying dislocations in single-crystal silicon, Dash[55] proposed an ingenious method based on the deposition of copper on the dislocations, and the observation of the dislocations decorated in this way, using an infrared technique. The essence of this method is as follows. Before the deposition of the copper the silicon plate was etched in a solution consisting of 1 part hydrofluoric, 3 parts nitric, and 10 parts acetic acid. Then copper was deposited on the etched surface from a solution of $Cu(NO_3)_2$. The specimen covered with copper was next heated for an hour in a hydrogen atmosphere at 900° C, and then cooled, taking several minutes to attain room temperature. The specimen was then polished and studied in infrared light. The principle of the apparatus for observing dislocations in this way is shown schematically in Fig. 5. Dash showed by the decoration method that every etch pit on the surface is formed where a dislocation line intersects it. With the aid of this method it is possible to study the interaction of dislocations in crystals and also other phenomena associated with them.

Meckel and Swalin[58] used etching by cathode sputtering to display screw dislocations in germanium. The surface of the germanium was bombarded by argon ions at a potential of 300 v and a pressure of 50 mm Hg. As a result of such bombardment, hillocks with spiral apices appear on the germanium.

Apart from those considered above, other ways of revealing dislocations also exist. For example, Tyler and Dash[57] studied a row of dislocations in deformed germanium using the diffusion of lithium and etching.

It should be pointed out in conclusion that the most widely used methods of displaying and studying dislocations, particularly "grown-in" dislocations, are the metallographic method, the x-ray method with a two-crystal spectrometer, and for silicon the decoration method. In order to obtain a general idea of the distribution of dislocations, it is necessary to combine these methods, since they complement one another. Thus, for example, very interesting results have been obtained by Dash[11] when studying the conditions for growing dislocation-free single crystals of silicon. In this work the author used both the metallographic method and decoration to display the dislocations.

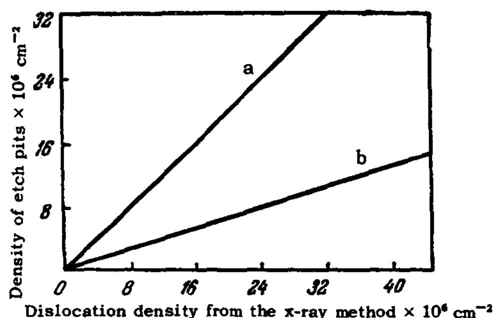

FIG. 4. Comparative results of dislocation density determinations by the metallographic and x-ray methods: a) theoretical curve corresponding to equal density by both methods, b) experimental curve corresponding to a reduced density by the metallographic method.

THE GENERATION OF DISLOCATIONS IN THE PROCESS OF CRYSTAL GROWTH FROM THE MELT

It is known that the dislocation density arising in semiconductor single crystals during growth depends

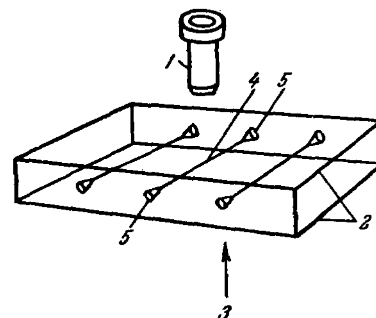

FIG. 5. Schematic diagram of the apparatus for observing dislocations in infrared light using the decoration method: 1 – microscope, 2 – optically polished surface, 3 – direction of light, 4 – line of deposited copper, 5 – etch pits.

on their conditions of growth.[58–65] The following mechanisms have been proposed for the generation of dislocations during the growth of single crystals:

1) plastic deformation caused by non-uniform cooling and annealing of the crystal;[40]

2) the formation of disc-shaped aggregates of vacancies in the crystal near the crystallization front, and their subsequent collapse to form dislocation loops;[66]

3) the capture of impurities exceeding the limit of solubility;[67]

4) the propagation of dislocations from the seed;[11]

5) fluctuations in the growth rate, which form adjacent layers in the crystal with differing lattice parameters, as a consequence of which dislocations arise at the boundaries of the layers.[68]

The Generation of Dislocations during Plastic Deformation. Germanium is extraordinarily brittle, as is silicon below 400° C. Fracture by cleavage along {111} planes usually occurs if the stress in the crystal exceeds[69] 20 kg/mm^2.

Germanium deforms plastically at temperatures above 500° C by slipping[10] along <110> directions in {111} planes when the component of shear in such a system exceeds a critical value that depends on the temperature. Slip occurs only in narrow regions parallel to the glide planes and it is assumed that dislocations form in them by the Frank-Read mechanism. On increasing the temperature plastic deformation occurs for lower values of the critical stress. Associated with the increased mobility of dislocations, the slip lines become less sharp.

Penning[70] has calculated the distribution of stress in a cylindrical isotropic crystal slowly cooled (surrounded by hydrogen) with radial outflow of heat. He obtained the following expressions for the stresses in polar coordinates:

$$\left.\begin{aligned} \sigma &= \left(4\frac{r^2}{R^2}-2\right)\sigma_0, \\ \sigma_\theta &= \left(3\frac{r^2}{R^2}-1\right)\sigma_0, \end{aligned}\right\} \quad (13)$$

$$\sigma_r = \left(\frac{r^2}{R^2}-1\right)\sigma_0, \quad (14)$$

where

$$\sigma_0 = 1/8hR\frac{\alpha E T_0}{1-\nu}\exp\left(-2h\frac{k}{R}t\right), \quad (15)$$

h is a constant determining the rate of cooling, T_0 is the original temperature, R is the radius of the bar, k is the thermal conductivity of germanium, $\alpha = 6 \times 10^{-6}$ °C/cm, $E = 1.2 \times 10^4$ kg/mm^2, $\nu = 0.28$. Since we are only interested in plastic flow, we can leave out of the normal stresses the hydrostatic component σ_0; we then obtain two remaining stresses: $\sigma'_{rr} = \sigma_r - \sigma_\theta$ and $\sigma'_{zz} = \sigma_z - \sigma_\theta$ in the radial and axial directions (they are shown in Fig. 6). It is seen from the figure that the stresses causing plastic flow give a radial compression of the crystal at the surface and an axial compression in the center. It should be remembered that plastic deformation takes place under compression either parallel or perpendicular to the glide planes, i.e., the {111} planes. To verify the theoretical calculations, Penning carried out the following experiments. A cylindrical bar of germanium was heated to a high temperature and then cooled in a current of hydrogen. The outflow of heat in the central part of the bar was mainly radial, but at the ends of the bar was axial and radial. In the parts of the ingot where radial cooling predominated, Penning observed in a section of the crystal on the {111} plane a non-uniform distribution of etch pits. A characteristic ring-shaped band with a different density of etch pits was observed between the center and the periphery of the crystal. The form of similar bands depended on the orientation of the specimens. Where simultaneous radial and axial cooling occurred, regions arose in the section of the ingot with a small density of dislocations which took the form of triangles with clearly expressed minima at the vertices.

Billig[40] proposes that under a radial temperature gradient the ingot cannot expand equally, and compressions are experienced in places. If the compressions exceed the elastic limit dislocations arise. The density of dislocations is approximately given by the expression

$$N_d = \frac{\alpha}{b}\frac{\partial T}{\partial r}, \quad (16)$$

where α is the thermal expansion coefficient of germanium, b is the Burgers vector.

Billig noted that in cases where the transition from the seed to the maximum diameter was sharp, the density of etch pits at the beginning was greater than where this transition occurred more smoothly. Billig supposes that the glide planes arise during extraction at the surface of the crystal, i.e., at the edge of the crystallization front, where the thermal stresses are greatest. From there they penetrate into the interior of the hot crystal, which is in the plastic deformation temperature region. Well-defined slip bands also arise when there is a sudden change of the temperature distribution. The rate at which the crystal cools, which governs the value of the radial temperature gradient attained in the bar, is given by:

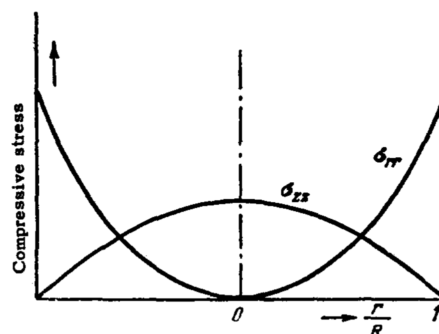

FIG. 6. The effective stresses causing plastic deformation of a cylindrical rod for radial outflow of heat: σ_{rr} – stresses in the radial direction, σ_{zz} – stresses in the axial direction.

$$\frac{dT}{dt} = \frac{2k}{3cR}\frac{dT}{dr}, \quad (17)$$

where k is the thermal conductivity, s is the specific thermal capacity, R is the radius of the bar.

Indenbom[71] has criticized Billig's conclusion on the importance of the radial temperature gradient in creating dislocations during the growth of crystals, and has proposed that dislocations are created due to the axial temperature gradient, with the radial gradient having only a second order effect. He considers that in the growing layer the interatomic distances should correspond to the temperature of crystallization, while the interatomic distances in the substrate layer depend not only on crystallization temperature, but also on the distribution of temperature in the depth of the crystal. Because of this, the atomic density in the growing layer is smaller than in the substrate, and some of the atomic planes in it are broken, forming dislocations, the density of which depends on the axial gradient. The density of dislocations as a function of the axial gradient is in this case given by the following formula:

$$N_d = \frac{a}{b}\frac{\partial T}{\partial n}. \quad (18)$$

Rosi[59] has studied the dependence of the dislocation density on the magnitude of the axial gradient. It follows from his experiments that a significant increase of the dislocation density occurs, as the value of the axial gradient is increased, at values of 200 — 220 deg/cm. The density of dislocations in crystals grown in this gradient was $(2-4)\times 10^3$ cm^{-2}.

Rosi has also studied the effect of the diameter of the crystal on the dislocation density. Crystals of 6 mm diameter grown in an axial temperature gradient of 150°C/cm had a dislocation density of 10 cm^{-2}, whereas a crystal of diameter 29 mm for the same value of the axial gradient had a dislocation density of 7×10^4 cm^{-2}. On this basis the author concluded that the radial gradient has a more powerful effect on the dislocation density than the axial gradient.

From Wagner's work[72] it follows that the dislocations arise not during growth, but owing to thermal shock after the growth of the crystal. Wagner does not give the values of the temperature gradient for the occurrence of dislocations in the growing crystal. It seems to us that this assertion of Wagner's is unfounded, since he apparently measured only the axial gradient and did not take into account the effect of the radial gradient. The diameters of the single crystals he grew were 15 — 20 mm. It is naturally very difficult to obtain a plane crystallization front for which the radial gradient is zero in such crystals. In reference 72 the smallest dislocation density in a single crystal was of the order 10^4 cm^{-2}. This indicates that the radial temperature gradient in Wagner's single crystals was quite high, whilst the axial gradient was small (about 10°C/cm).

Dash's studies[55] show that the temperature gradient has a marked effect on the formation of dislocations in silicon single crystals if the crystal already contains dislocations. If the crystal contains no dislocations it can withstand not only large temperature gradients, but thermal shock as well.

The Creation of Dislocations through Collapse of Disc-shaped Vacancy Aggregates. This mechanism for the creation of dislocations was proposed by Frank.[74] In essence it is as follows. If the crystal is growing in a large axial gradient, it can freeze in at the crystallization front an accumulation of vacancies. We suppose that the crystal is growing in the [111] direction. The vacancy aggregates will have minimum surface energy when they are bounded by {111} planes, at which there are unsaturated covalent bonds on the sides directed towards the aggregate.

The investigations of Ellis[36] and Dash[55] do not support the suggestion that dislocations form by the collapse of disc-shaped aggregates of vacancies in germanium.

The Creation of Dislocations through Capture of an Increased Impurity Concentration by the Growing Crystal. The capture in a growing crystal of a locally increased impurity concentration changes the lattice parameters in this region, because the atomic radii of the impurities differ from that of the solvent. The greater this difference, the smaller the impurity concentration needed to change the lattice parameters. At the boundaries of adjacent regions with differing lattice parameters quite large stresses can arise which cause the formation of dislocations. Alekseeva[73] showed that the density of dislocations in germanium increases rapidly if the concentration of bismuth in it attains the solubility limit. Dislocations diminish these stresses to some extent.

The Creation of Dislocations by Propagation from the Seed. Dash's work[61] on the production of dislocation-free single crystals of silicon showed that the degree of perfection of the seed has a very great effect on the perfection of the growing crystal. In a single crystal of silicon he has shown an example of how dislocations can promote the formation of further dislocations in the growing crystal under thermal stresses by the Frank-Read mechanism.

In conclusion, it should be pointed out that the process of dislocation formation in a growing crystal is very complicated, and it is impossible to say which of the mechanisms enumerated above is the principal one. It seems very likely that several mechanisms act simultaneously. Consequently, when growing dislocation-free single crystals of semiconductors, one must try to attain the minimum effect due to the various factors.

THE EFFECT OF DISLOCATIONS ON THE CHARACTERISTICS OF SEMICONDUCTOR DEVICES

It is well known that many electrical properties of semiconductor devices depend on the quality of the semiconductor crystals used in them. There are no detailed studies in the literature describing the effect of dislocations on the characteristics of semiconductor devices. It is obvious that to obtain some types of high-quality semiconductor devices, semiconductor crystals must be used which have perfect crystal lattices. Billig[40] mentions that the magnitude of the inverse voltage diminishes as the density of dislocations in germanium increases. It follows therefore that to fabricate semiconductor devices with large inverse voltages, semiconductor crystals with minimum dislocation densities must be used.

Frank[74-75] has shown that the diffusion of copper in bulk germanium having a perfect structure occurs much more slowly than along dislocation lines. Studies of the diffusion of impurities in germanium and silicon[76-80] have shown that impurity atoms diffuse along edge dislocation lines more rapidly than in the rest of the germanium volume. This effect is apparently very important during the fabrication of high-voltage diffused transistors, since, because of the different speeds of diffusion along dislocation lines and through the perfect bulk crystal, the diffusion front has spikes where dislocation lines intersect it. The resulting p-n junction has the same form.

The presence of sharp projections at the p-n junction can create high electric fields, which can lead to the electrical breakdown of the p-n junction. The presence of dislocations in the starting material causes the generation of new dislocations during the diffusion process, or when the crystal is cooled, after diffusion, from high temperatures to temperatures below the plastic deformation region. The creation of new dislocations can, of course, also cause a deterioration in the characteristics of the finished device.

Oberly[81] has shown that during electrical etching the places where dislocations emerge on the surface etch more rapidly. Hence it is very difficult to fabricate sufficiently good surface barrier transistors from material having a high dislocation density.

[1] A. R. Verma, Phil. Mag. **42**, 1005 (1951).
[2] Vogel, Pfann, Corey, and Thomas, Phys. Rev. **90**, 489 (1953).
[3] W. C. Dash, J. Appl. Phys. **27**, 1193 (1956).
[4] A. J. Forty, The Direct Observation of Dislocations in Crystals (Russ. Transl.), M. Mettallurgizdat, 26 (1958).
[5] W. T. Read, Dislocations in Crystals (Russ. Transl.) M. Metallurgizdat, 279 (1958).
[6] A. H. Cottrell, Dislocations and Plastic Flow in Crystals (Russ. Transl.), M. Metallurgizdat, 267 (1958).
[7] I. A. Oding, Теория дислокации в металлах и ее применение (The Theory of Dislocations in Metals and its Application), Acad. Sci. Press 84 (1959).
[8] V. L. Indenbom, Кристаллография **3**, 113 (1958), Soviet Phys.-Crystallography **3**, 112 (1959).
[9] E. Yu. Kokorish in "Рост кристаллов" (The Growth of Crystals) Vol. II, Acad. Sci. Press, 221 (1959).
[10] Regel', Urusovskaya, and Kolomiichuk, Кристаллография **4**, 937 (1959), Soviet Phys.-Crystallography **4**, 895 (1960).
[11] W. C. Dash, Growth and Perfection of Crystals, (John Wiley and Sons, Inc., New York, 1958), p. 361.
[12] J. Hornstra, J. Phys. Chem. Solids **5**, 129 (1958).
[13] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).
[14] A. D. Kurtz and S. A. Kulin, Acta Met. **2**, 352 (1945).
[15] W. Shockley, Phys. Rev. **91**, 228 (1954).
[16] W. T. Read, Phil. Mag. **45**, 775 (1954).
[17] W. T. Read, Phil. Mag. **45**, 1119 (1954).
[18] W. T. Read, Phil. Mag. **46**, 111 (1955).
[19] C. J. Gallagher, Phys. Rev. **88**, 721 (1952).
[20] Pearson, Read, and Morin, Phys. Rev. **93**, 666 (1954).
[21] W. C. Ellis and E. S. Greiner, Phys. Rev. **92**, 1061 (1953).
[22] G. Gallagher and A. Tweet, Phys. Rev. **96**, 834 (1954).
[23] Greiner, Breidt, Hobstetter, and Ellis, J. Metals **7**, pt. 2, 813 (1957).
[24] F. L. Vogel, J. Metals **8**, pt. 2, 946 (1956).
[25] A. Tweet, Phys. Rev. **99**, 1245 (1955).
[26] G. K. Wertheim and G. L. Pearson, Phys. Rev. **107**, 694 (1957).
[27] J. P. McKelvey, Phys. Rev. **106**, 910 (1957).
[28] S. R. Morrison, Phys. Rev. **104**, 619 (1956).
[29] C. Benoit à la Guillaume, J. Phys. Chem. Solids **8**, 150 (1959).
[30] A. Kobus, Elektronika **4**, 141 (1958).
[31] Kurtz, Kulin, and Averbach, Phys. Rev. **101**, 1285 (1956).
[32] R. R. Hasiguti and E. Matsura, J. Phys. Soc. Japan **12**, 1347 (1957).
[33] J. Okada, J. Phys. Soc. Japan **10**, 1110 (1955).
[34] J. W. Allen, J. Electronics **1**, 580 (1956).
[35] L. S. Milevskiĭ, Кристаллография **4**, 785 (1959), Soviet Phys.-Crystallography **4**, 743 (1960).
[36] S. G. Ellis, J. Appl. Phys. **26**, 1140 (1955).
[37] S. G. Ellis, Transistors-I, RCA Laboratories 1956, p. 97.
[38] Bardsley, Bell, and Straughan, J. Electronics and Control **5**, 19 (1958).
[39] W. G. Pfann and R. L. Vogel, Acta Met. **5**, 377 (1957).
[40] E. Billig, Proc. Soc. (London) **A235**, 37 (1956).
[41] Rhodes, Batsford, and Dane-Thomas, J. Electronics and Control Sec. 1, **3**, 403 (1957).
[42] W. C. Dash, J. Appl. Phys. **27**, 1193 (1956).
[43] N. N. Sirota and A. V. Shibaeva, Инж.-физ. ж. (Eng.-Phys. J.) **2**, 57 (1959).

[44] Johnston, Li, and Knudson, J. Appl. Phys. **28**, 746 (1957).
[45] O. Rösner, Z. Metallkunde **46**, 225 (1956).
[46] I. I. Oberly, J. Metals **6**, 1025 (1954).
[47] W. Bardsley and B. W. Straughan, J. Electronics **1**, 561 (1956).
[48] Y. Matukura and T. Suzuki, J. Phys. Soc. Japan **12**, 976 (1957).
[49] Goss, Benson, and Pfann, Acta Met. **4**, 332 (1958).
[50] W. A. Tiller, J. Appl. Phys. **29**, 611 (1958).
[51] R. E. Maringer, J. Appl. Phys. **29**, 1261 (1958).
[52] A. R. Lang, J. Appl. Phys. **29**, 597 (1958).
[53] U. Bonse and E. Koppler, Z. Naturforsch. **13a**, 348 (1958).
[54] J. B. Newkirk, Phys. Rev. **110**, 1465 (1958).
[55] W. C. Dash in "Dislocations and Mechanical Properties of Crystals" N.Y. 1957, p. 57.
[56] B. B. Meckel and R. A. Swalin, J. Appl. Phys. **30**, 89 (1959).
[57] W. W. Tyler and W. C. Dash, J. Appl. Phys. **28**, 1221 (1957).
[58] H. Dorendorf, Z. Angew. Phys. einschl. in Nucleonik **9**, 513 (1957).
[59] F. D. Rosi, RCA Review **19**, 349 (1958).
[60] E. Yu. Kokorish, op. cit. ref. 9, p. 120.
[61] W. C. Dash, J. Appl. Phys. **30**, 459 (1959).
[62] F. C. Frank, Verformung und Fliessen des Festkörpers, Berlin, Springer Verlag, 1956, pp. 73-78.
[63] P. Penning, Phillips Res. Rep. **13**, 79 (1958).
[64] D. C. Bennett and B. Sawyer, Bell Syst. Techn. J. **35**, 637 (1956).
[65] I. G. Cressell and J. A. Powell, Progress in Semiconductors, Vol. 2, (Heywood and Co., London, 1957), p. 137.
[66] E. Teghtsoonian and B. Chalmers, Can. J. Phys. **30**, 388 (1952).
[67] R. Newmann and W. W. Tyler, Phys. Rev. **96**, 882 (1954).
[68] W. Tiller, J. Appl. Phys. **29**, 611 (1958).
[69] Buerin, Hornstra, and Penning, Nuovo cimento, suppl. **7**, No. 2, 646 (1958).
[70] P. Penning, Phillips Techn. Rev. **19**, 357 (1957/1958).
[71] V. L. Indenbom, Kristallografia **2**, 594 (1957).
[72] R. S. Wagner, J. Appl. Phys. **29**, 1679 (1958).
[73] V. G. Alekseeva and P. G. Eliseev, Физ. твердого тела **1**, 1304 (1959), Soviet Phys.-Solid State **1**, 1195 (1960).
[74] F. C. Frank, Dislocations and Mechanical Properties of Crystals N.Y. — London 1957, p. 408.
[75] F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).
[76] C. S. Fuller and J. A. Ditzenberger, J. Appl. Phys. **28**, 40 (1957).
[77] J. A. Pankove, J. Appl. Phys. **28**, 1054 (1957).
[78] F. Karstensen, J. Electronics and Control **3**, 305 (1957).
[79] D. Turnbull and R. E. Hoffman, Acta Met. **2**, 419 (1954).
[80] A. G. Chynoweth and G. L. Pearson, J. Appl. Phys. **29**, 1103 (1958).
[81] J. Oberly, Acta Met. **5**, 122 (1957).

Translated by K. F. Hulme