PHYSICAL REVIEW B VOLUME 17, NUMBER 8 15 APRIL 1978

Formation of interstitial-type dislocation loops in tetrahedral semiconductors by precipitation of vacancies

J. A. Van Vechten
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 14 November 1977)

It is hypothesized that when vacancies precipitate to form voids in tetrahedral semiconductors, e.g., Si and GaAs, reconstruction reactions occur on the internal surfaces of these voids in the same manner as they are observed to occur on external surfaces of the same crystallographic orientation. Previously, it has been concluded that many of the various reconstruction reactions observed on various semiconductor surfaces produce hillocks by expelling a portion of the atoms from the unreconstructed (ideal) surface to migrate in a reaction front across the surface. From these two lemmas, it is here concluded that the corresponding waves of atoms driven by reconstruction on internal surfaces will precipitate into pillars of crystal-line material within the void and produce dislocation loops at which the lattice planes bow away from the center. Such dislocations are conventionally denoted "interstitial type." This mechanism may explain several observations of "interstitial type" dislocations in semiconductors, including Si and GaAs, for which there is much evidence for vacancies and no other evidence for self-interstitials.

I. INTRODUCTION: VACANCIES OR INTERSTITIALS?

Surely the most fundamental question to resolve when one begins the study of deep point defects and line defects in semiconductors is whether the dominant native defect involved in the formation and motion of the observed defects is the vacancy or the self-interstitial. Despite this fact and the intensive study of deep point and of line defects in several semiconductors over many years, this question is still being debated even for the most thoroughly studied cases. For example, in the case of Si, Refs. 1–6 refer to a few of the recent papers in which the respective authors interpret diffusion and formation of dislocations and stacking faults in terms of vacancies, while Refs. 7–12 refer to a few of the recent papers in which these phenomena are described in terms of Si self-interstitials. A similar situation exists in GaAs-AlGaAs, where some authors explain the formation of dark-line defects in heterostructure lasers entirely in terms of vacancies,[13,14] while others[15,16] invoke self-interstitials to explain their formation.

Those who believe that vacancies are the dominant native defects in group IV and III-V semiconductors do so for several reasons: (i) Only vacancies and vacancy complexes are identified by electron paramagnetic resonance in these materials even when they have been subject to electron irradiation and one may be certain that vacancy-interstitial (Frenkel) pairs were produced.[17] The absence of self-interstitials in irradiated samples has generally been ascribed to a rapid athermal migration of self-interstitials,[18] even at 2 K, and to a very large heat of formation of interstitials,[19] which provides a large driving force for their removal. (ii) Several impurities, such as Zn in GaAs,[20] are observed to diffuse as interstitials but to occupy predominantly substitutional sites. Therefore, there must be vacant lattice sites for them to occupy. (iii) Diffusion and related phenomena are successfully described by ascribing multiple ionization levels to the native defect which are the same as those observed for the vacancy in low-temperature irradiation experiments.[4,21,22] (iv) Theoretical estimates of the heat of formation of vacancies correspond well with those of the native defect observed in quenching and diffusion experiments.[21-25] As the threshold energies for Frenkel pairs in irradiation experiments are quite high, the energy to be ascribed to the heat of formation of the interstitial is much higher than that of the vacancy.[19] This is also in agreement with simple theoretical arguments.[19]

Those who believe that self-interstitials are the dominant native defects in these same group IV and III-V semiconductors do so mainly because the great majority of dislocation loops and stacking faults observed by transmission electron microscopy (TEM) in these materials have been determined to be of extrinsic or "interstitial" character.[7-12,15,16,26,27] Although four mechanisms by which interstitial-type dislocations may be formed without any self-interstitials being present are well established[1] (and discussed in Sec. II), these authors feel that in several cases these four alternative mechanisms do not obtain and that the only remaining mechanism is the precipitation of self-interstitials.

The purpose of the present paper is to analyze

 © 1978 The American Physical Society

(Sec. III) the mechanism by which dislocations should be expected to form if indeed vacancies are much more numerous than self-interstitials in these semiconductors. It is concluded that, because reconstruction should occur on interior surfaces as it is known to occur on exterior surfaces, the precipitation of vacancies will cause the formation of interstitial-type dislocations in most, but not all, experimental situations. The possibilities to verify this contention experimentally are discussed in Sec. IV.

The author is aware that his proposal is at odds with the conventional wisdom of the TEM-dislocation community. He maintains that it is a reasonable conclusion from what is generally accepted in high-vacuum surface science and the most attractive resolution of the dilemma of the evidence for vacancies and for self-interstitials where it is clear that they cannot both be present in significant concentrations.

II. WHAT AN "INTERSTITIAL-TYPE" DISLOCATION LOOP IS

When an electron microscopist says that a dislocation loop is "interstitial-type", he means that the host-lattice planes bow away from the center of the loop.[28] When he says the dislocation loop is "vacancy type", he means that the host-lattice planes bow toward the center of the loop (see Fig. 1). This notation was popularized by Friedel,[28] who observed that if a number of vacancies were to condense to form a planar void of sufficient size, then it would be energetically favorable for the material to remove the void by rewelding the surface on either side together. This would remove the surface energy of the void over its entire extent at the cost of deforming the lattice inward only around the perimeter. Thus, it is clear that for a sufficiently large number of vacancies in a cluster, the rewelding will reduce the total energy of the solid. It should also be clear that there will always be an activation barrier to be overcome before this rewelding can occur, because the opposite planes must be brought together. Furthermore, if foreign atoms, such as H, He, or Ar, in the presence of which crystals are often grown, precipitate into the void, they may prevent the rewelding from occuring.

It should be emphasized that the electron microscope detects the bowing of the lattice planes rather than the presence or absence of host atoms. In the absence of lattice distortion, a vacancy would have a scattering potential for electrons differing from that of an interstitial of the same atomic species only by a sign.[29] (The potential being that of the atom.) As the image intensity is proportional to the square of the electronic wave function, the image contrast produced by vacancies is the same as that produced by interstitial atoms. While it is true that the electron beam is less attenuated in passing through vacancies than in passing through interstitials, the difference of one atomic layer more or less in a sample typically 1 μm thick is generally not detectable and would be masked by steps and adsorbed layers on the surface of the sample.

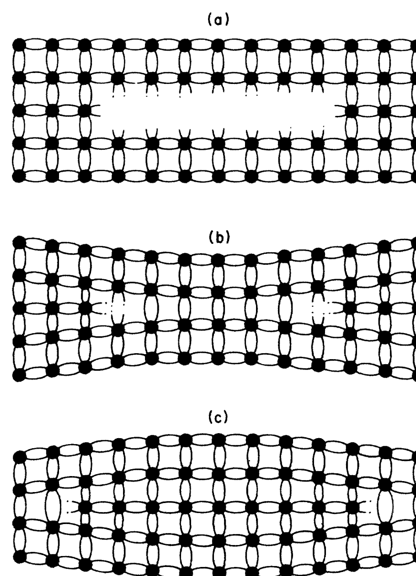

FIG. 1. Schematic representation of the conventional view of the conversion of a cluster of vacancies (a) into a "vacancy-type" dislocation loop (b) by a rewelding of the surfaces on either side of the void. (These figures are adapted from Friedel, Ref. 28). In (c) we see an "interstitial-type" dislocation loop at which the host-lattice planes bow away from the center of the loop as would be expected if, for example, self-interstitials were to precipitate.

Now, it has long been recognized that the fact that a dislocation loop is determined to be "interstitial-type" does not imply that it was formed by a precipitation of self-interstitials.[1] Indeed, four alternative processes have been firmly established in the semiconductor literature. One alternative process, which has been widely observed in Si, is the conversion of interstitially diffusing impurities (typically Cu, Au, or Li) into substitutional impurities by absorption into interstitial loops.[30-33] A second process is the emission of vacancies by an interstitial loop initially present.[14,34] The interstitial loop grows by one atom for each vacancy that is emitted from its boundary and diffuses away. In a third mechanism,[35] a precipitate particle (e.g., Cu or Fe in Si[5,6]) is formed at an edge dislocation. Compressive stress inside the pre-

cipitate is relieved by flow of vacancies from the dislocation to the precipitate particle. This flow may take place by dislocation pipe diffusion or volume diffusion and is accompanied by dislocation climb. The sense of the climb is such that an interstitial loop will grow and a vacancy loop will shrink.[5,6,35,36] A fourth mechanism is prismatic punching,[37-39] which is only rarely observed in semiconductor crystals that have not been mechanically damaged.[39]

There is a fifth alternative mechanism which has not been much discussed in the literature. Because these semiconductors expand on solidification, any inclusion of the liquid phase that may be trapped in the solid during crystal growth will tend to punch out interstitial-type dislocations when it does freeze.[40,41] One expects inclusions to occur when the crystal is growing by means of reentrant growth steps. When the growth steps are more than a few atomic layers high (on covalent crystals they are often several hundreds of layers high), one would expect[42,43] to find reentrant growth steps even if the treads of the growing surfaces of the crystal do not reconstruct. The tendency to form reentrant growth steps would be much increased if these treads do reconstruct.[41]

This fifth alternative mechanism has the attraction that it would provide a mechanism for the nucleation of dislocations in crystals of such high purity that impurity induced heterogeneous nucleation is not effective. It has been noted that the homogeneous nucleation of a dislocation from a concentration of single vacancies that was at equilibrium with the surface during crystal growth is normally an extremely unlikely event.[44,45] If one assumes the self-interstitial is the dominant native lattice defect, the same considerations as presented in Refs. 44 and 45 show that the homogeneous nucleation of an interstitial dislocation is equally unlikely. It is usually concluded that almost all observed dislocations were heterogeneously nucleated by impurity precipitates, but many semiconductors are grown so pure that this assumption should be questioned.

III. RECONSTRUCTION ON INTERNAL SURFACES

Reconstruction reactions are first-order phase transitions that are observed (in high vacuum) on most low index [e.g., (100), (110), and (111)] surfaces of group IV and III-V semiconductors by low-energy-electron diffraction (LEED), photoemission (PE), and other techniques.[46-53] It is generally agreed that these reactions occur because covalently bonded crystals can lower their free energy by removing the dangling bonds on the ideal surface (i.e., that obtained by simply truncating the bulk crystal structure) by switching to a new crystal structure for the surface layer of atoms. Whereas the atoms in the bulk of these semiconductors engage in s-p^3 hybridized bonding, those on the surface may engage in s-p^2 hybridized bonding or p bonding or some other type of bonding in order to minimize their free energy.

The first lemma of the present hypothesis is that similar reconstruction reactions will occur on internal surfaces of a crystal that are formed by the precipitation of vacancies at voids, vacancy complexes, or dislocations, however nucleated. As long as the opposite sides of such cavities remain sufficiently far apart that the interaction between them is slight, these reconstructions will surely obtain. In order to gauge how great a separation between surfaces is sufficient, we note that surface energies result from the spilling of electron density into vacuum, where it cannot be compensated by atomic cores, which occurs because the electronic wave functions are not terminated abruptly at a surface.[23,25,54-57] This spilling of the charge density will be approximately

$$\rho(x)=\rho(0)\exp(-k_s x), \tag{1}$$

where k_s is the linearized Thomas-Fermi screening wave number. The important point is that, because the valence electron density of these semiconductors is very high, k_s is large and the spilled charge density falls off rapidly.[23,25,57] Indeed, for Si

$$k_s R_W = 3.5, \tag{2}$$

where R_W is the Wigner-Seitz radius. Therefore, as long as the opposite surfaces of an internal cavity remain at least one atomic spacing apart, there is negligible interaction between them. In fact, $2R_W$ is a conservative estimate of the distance between opposite surfaces because atoms move away from the vacuum and toward the bulk immediately upon formation of the surface, before any further reconstruction can occur, and also around single vacancies. This is simply because charge is redistributed from the dangling bonds of these surfaces to the back bonds causing them to shorten.[23,25,52,58]

It should be noted that a minimum extent of surface area is required before reconstruction can occur. Empirically,[59] the minimal dimension D_c is typically 6–8 nm. The rate at which the reconstruction reaction occurs increases with increasing extent of the surface.[51,60] This variation has been shown to fit the hypothesis that once the reconstruction reaction starts on any tread of a stepped surface, it propagates rapidly across the entire tread to the risers.[60] This fact has been explained[41,60,61] by the hy-

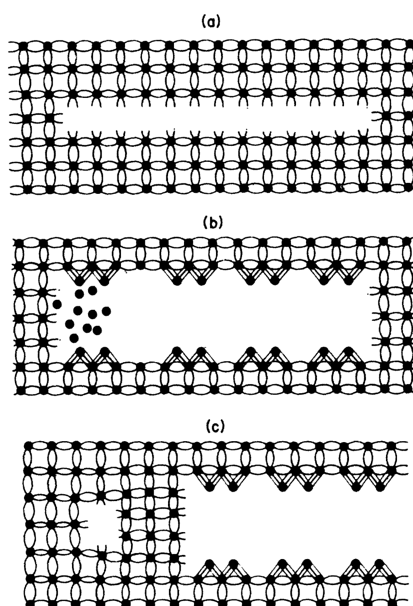

FIG. 2. Schematic representation of the author's proposal of a mechanism for the conversion of a planar precipitate of vacancies into an "interstitial-type" dislocation loop by the reconstruction of the surfaces of the cavity. In (a) we again see the cavity formed by the precipitation of vacancies, as in Fig. 1(a). In (b) both surfaces of the cavity are undergoing the surface reconstruction reaction which drives a wave of atoms, that are expelled from the surfaces by the reaction, into the extremities of the cavity. These extra atoms in the extremities are thought to be in a state similar to that of the liquid phase. The reconstructed surface is a phase of lower energy, lower density, and different bonding. In (c) the atoms that were expelled by the reconstruction have recrystallized to the bulk crystal structure. As they do so, they expand, as does the liquid phase, so that an interstitial-type dislocation loop is formed, the surfaces of the original cavity are forced apart by one lattice spacing, and a pillar of good crystalline material is left to stabilize the cavity and the dislocation.

pothesis that reconstructed surface phases generally contain fewer atoms than the ideal (unreconstructed) surface phase,[46,47,52,53] so that the reaction releases atoms and drives them in a reaction front that perturbs the metastable ideal phase and thus propagates the reaction further. When this occurs on an exterior surface of a crystal, one would expect the waves of released atoms to collide and produce hillocks. This effect has evidently been observed; the hillocks on Si being typically 40 nm high.[62] It provides an explanation for the continuous source of steps, that is required for crystal growth, in the absence of screw dislocations.[41,61]

Although the structure and coordination of the released atoms as they propagate in the wave has not been determined, it is here assumed that, as in the liquid phase, these atoms are more densely packed than in the tetrahedrally coordinated solid phase. It would seem that if the atoms were tetrahedrally coordinated in the covalent solid phase, they would not be able to migrate across the surface as required to explain the kinetics of the reconstruction on stepped surfaces.[51,60] In any case, the tetrahedral phase is the least dense of all known condensed phases of these compositions. This point is important because it implies that these atoms will expand, as does a liquid drop, when they recrystallize to the bulk solid phase.

The second lemma of the present hypothesis is the contention just introduced that reconstruction releases atoms from the ideal surface, that these will migrate in a wave across the flat surface until stopped for some reason whereupon they solidify to the bulk crystal structure and expand to produce a hillock, pillar, or similar surface defect.

Now let us consider what should happen as vacancies precipitate in the interior of a covalent crystal. It is well known that there is a binding energy of order 1 eV between vacancies[57,63,64] so that they will form multiple vacancy clusters (small voids) as the crystal cools from its growth temperature. Suppose that an approximately disk-shaped cluster (cavity) has grown to a size sufficient to have a low index surface greater than the critical extent, 6–8 nm, required for reconstruction[59] without rewelding (see Fig. 2). When the reconstruction occurs, it produces a wave of atoms which propagates through the void across the interior surface. The wave will stop when it collides with another wave, the end of the cavity, or perhaps a patch of reconstructed surface. Thereupon, the atoms solidify into the bulk solid phase. Obviously, an internal hillock or pillar produced inside the cavity of precipitated vacancies could not be as high as the 40-nm ones on exterior surfaces. One might instead suppose these atoms recrystallize as would a drop of the liquid, expanding as it solidifies and tending to drive the opposite surfaces of the cavity apart by one or a few atomic spacings. If this does occur, then an "interstitial-type" dislocation loop is produced in which the "extra plane" of lattice sites contains regions where host atoms are present and regions where they are not (see Fig. 3). Where the atoms are not present, the opposite surfaces are now reconstructed, so that there are no dangling bonds and there is a much larger activation barrier against rewelding.

Several questions regarding this hypothesis come to mind: (i) Is the proportion of pillar regions to void regions likely to be sufficient to stabilize the dislocation loop? (ii) Is the Burgers vector of the

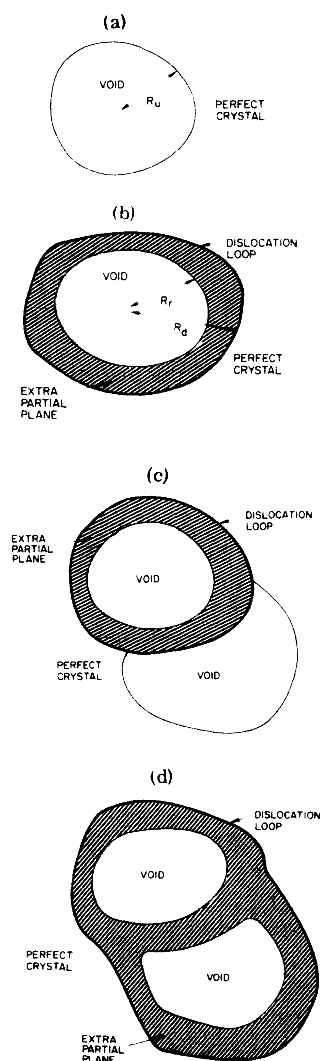

FIG. 3. Proposed process, as in Fig. 2, viewed normal to the plane of the cavity and of the loop. In (a) we see the original disk-shaped cavity produced by the vacancies prior to its reconstruction. In (b) the cavity has reconstructed and formed a pillar between the dislocation loop and the reconstructed cavity from the atoms expelled by the reconstruction reaction. In (c) more vacancies have precipitated out of the bulk to form a new unreconstructed void at the perimeter of the first dislocation loop. The vacancies are attracted to this region by the tensile strain field there. They do not annihilate the pillar because of the compressive strain field in that region. In (d) the new cavity has undergone reconstruction producing more pillar region and increasing the dislocation loop.

dislocation necessarily the same as the orientation of the cavity surface which reconstructed? (iii) How about the problem of nucleating such a dislocation in the first place? (iv) If such a dislocation were nucleated, would it grow? (v) Is the energy released by reconstructing the internal surface greater than that consumed producing the dislocation? (vi) Under what circumstances would vacancy type dislocations be expected instead? Let us consider these questions in order.

(i) The generally accepted, Lander-Morrison model for the stable (7×7) reconstruction of the (111) surfaces of Si contains 26% fewer atoms than the ideal surface.[46,47] As there are two such surfaces to the vacancy produced cavity, 52 atoms would be released for every 100 vacancies precipitating into a disk-shaped cavity one atomic spacing thick. Let us suppose for the moment that the Burgers vector of the dislocation is the same as the orientation of the reconstructed surface. If the host lattice is forced apart one atomic layer to form a dislocation loop as these atoms solidify, then 26% of the extra plane of lattice sites would be occupied, i.e., 26% of the region would be pillar and 74% void. If the initial cavity is a disk two atomic spacings thick, 26 atoms would be released for every 100 vacancies precipitating and, if the host lattice is forced apart one spacing (so there are 3 layers where there were 2) to form the dislocation, then 15.3% of the loop would be pillar. If the initial cavity is a disk three atomic spacings thick, still 13.8% of the resultant dislocation loop would be pillar. This case is typical of the stable reconstructions that occur on the low index surface of most semiconductors.[52,53] It would seem that such proportions of pillar to void would be adequate to stabilize the loop.

(ii) It seems clear that the Burgers vector of the dislocation need not be the same as the orientation of the cavity surface which reconstructs. If a liquid inclusion were to solidify and to punch out dislocations, the resultant Burgers vectors would be determined by properties of the host as well as by the shape of the inclusion. Moreover, after the dislocation is nucleated, its Burgers vector may be rotated by low-energy processes,[65] such as reaction with Shockley partial dislocations.

(iii) In addition to the dislocations that may be nucleated by the action of impurities,[30-39] some interstitial-type dislocations would be nucleated in pure semiconductor crystals grown from a melt, which is more dense,[66] by the trapping of liquid inclusions by reentrant (overhanging) growth steps that are many atoms high.[41-43] Moreover, it is here proposed that the precipitation of vacancies-interior reconstruction mechanism will itself nucleate interstitial-type dislocations due to the expansion of the released atoms as they recrystallize, and that it will do so without requiring that the vacancy cluster first assume the unlikely shape of a disk one atomic layer

thick.[44,45] Suppose that the vacancies in Si precipitate to an octahedral-shaped cavity, which is the equilibrium shape of a cavity in Si. The dimensions of the (111) surfaces of this cavity exceed the minimal dimension for reconstruction[59] (about 6 nm) when about 5.1×10^3 vacancies precipitate into it. There will then be 1.1×10^3 atoms on the 8 surfaces bounding this cavity. If all surfaces reconstruct, 2.9×10^2 atoms will be released in the wave of the reaction front. Suppose that, before recrystallization, these atoms form a single drop in one corner of the octahedron so as to minimize their surface energy. It seems clear that recrystallization will begin where the drop contacts the surfaces of the cavity and will next occur on the free surface of the drop. As with the freezing of ice cubes, the interior of the drop will be the last to recrystallize. If the drop does expand about 15% in volume when it recrystallizes, as does the liquid phase,[66] it will stress the surrounding lattice. One of the ways in which this stress can be relieved is by the formation of an interstitial dislocation loop sufficient to contain about 30 atoms in its extra partial plane. Obviously this configuration would not be a state of minimum energy, but it is well known that dislocations are not equilibrium defects; they would never exist were the crystal at equilibrium.[67]

(iv) We now suppose that an interstitial-type dislocation loop has been nucleated by one of the above mechanisms and that vacancies diffuse to it. It is commonly stated that vacancies will annihilate such a dislocation. However, it is well known that impurity atoms form precipitates on and about dislocations as the crystal cools and their concentrations become supersaturated. Vacancies will generally not annihilate such precipitates because to do so would require redissolving the impurity atom into the solid from which it had precipitated. Vacancies should not be expected to annihilate the dislocation produced by or to accommodate such precipitates either. In those central portions of the loop where the extra partial plane is composed of host atoms, the arrival of vacancies from the bulk will not remove any lattice sites from the dislocation, i.e., annihilate it, unless the vacancies nucleate a disk-shaped cavity and reweld the opposing surfaces, which, as noted above, is a very unlikely event.[44,45] Evidently, there would be little attraction of vacancies to such regions of the loop and they would diffuse on through the bulk. In those central portions of an "interstitial-type" dislocation loop formed by the vacancy precipitation-surface reconstruction mechanism where the "extra partial plane" is in fact a cavity with reconstructed surfaces, the arrival of a vacancy from the bulk would merely convert that bulk vacancy into a vacancy in the reconstructed surface phase. The energy of formation of vacancies in the reconstructed surface phase is still undetermined, but it is certain to be greater than that in the unreconstructed surface phase, where it is of order 75% that in the bulk.[41,60] Therefore, there may be little attraction for vacancies to such regions. If so, they may not stay there. If they do persist on the reconstructed surfaces, they will eventually remove the layer of surface phase exposing the bulk phase beneath. When a sufficient extent of this ideal surface phase is exposed, it will reconstruct releasing more atoms and causing the dislocation and/or the pillar regions within it to grow. In either case, it seems that the arrival of vacancies will not cause these interstitial-type dislocation loops to dissolve. Thus, it is only on the perimeter of the loop at sites occupied by host atoms that there is any danger of vacancies annihilating the dislocation loop.

Let us now consider whether the arrival of vacancies from the bulk to the perimeter of the loop, the core of the dislocation, should cause the loop to shrink or to expand. Without knowing anything about the disposition of atoms in the core, which is not firmly established for these dislocations, we may be sure that for the present case of "interstitial-type" loops, the region immediately inside the perimeter is strained compressively and that the region immediately outside the perimeter is subject to large tensile strain. In order to reach the interior of the loop, vacancies would have to migrate through the regions of tensile strain. However, the vacancies will tend to remain and to cluster in the region of highest tensile strain because the energy of vacancy formation $\Delta H_f(V)$ is a decreasing function of the interatomic spacing r, and so is less in regions of tensile strain. This may be understood by using the approximation of the single vacancy as a macroscopic cavity[23,25,57,68] and estimating

$$\Delta H_f(V)=A\sigma, \tag{3}$$

where A is the surface area of the cavity and σ is the energy per unit area of the cavity surface. (Because the valence electron density is so high, as noted at Eq. (2), this is a rather good approximation in semiconductors,[23,25,57] although it is not very accurate for many metals.[68]) As A is proportional to r^2 while σ is proportional[56] to $r^{-5/2}$, Eq. (3) implies

$$\Delta H_f(V)=\text{const}\,r^{-1/2}. \tag{4}$$

One may also wish to consider the effect of breaking the covalent bonds. Several authors[69-71] have analyzed the bond bending and bond stretching

force constants between atoms. From these analyses, and from the observed signs of the third-order elastic constants, it is clear that the interatomic forces are decreasing functions of r. (One might also consider the chemical trends in the commonly accepted experimental values[23,25,57,72] for $\Delta H_f(V)$, which are greater for C than for Si and greater for Si than for Ge, etc.) Of course, some of the vacancies will pass through the regions of tensile strain to the interior perimeter of the loop despite this repulsion due to the strain field there. But before the compressive stress can be removed and the energy of the crystal reduced (as assumed by those who assert that vacancies will annihilate interstitial-type dislocations), it would be necessary to cluster a sufficient number of vacancies in the interior perimeter so that part of the extra partial plane there could be removed by the mechanism of rewelding of the surfaces of a disk-shaped cavity. Evidently, the probability of such an event in this case is even less than in regions without compressive strain.

Thus, we come to the conclusion that as vacancies arrive in the vicinity of the dislocation loop they will cluster predominately in the regions of highest tensile strain outside the loop. As they do so, they will produce extended cavities. The shape of these cavities will be influenced by the strain field outside the dislocation. While they will probably not be disks of thickness one atomic layer, they will probably also not have the equilibrium shape of cavities in the host lattice either. Consequently, when these cavities reach the critical extent, they will reconstruct releasing more atoms that will cause the dislocation to grow so that the process may be repeated until the supersaturation of vacancies is depleted.

(v) Referring to Fig. 3(a), we may estimate the energy of an initial approximately disk-shaped cavity before reconstruction as

$$E_1 = 2\pi R_u^2 \sigma_u, \tag{5}$$

where R_u is the radius of this cavity and σ_u is the energy per unit area of the unreconstructed surface. When reconstruction occurs, the surface energy is reduced to σ_r and the radius of the void region is reduced to R_r because a fraction of the atoms released from the surface fill up part of the cavity. The energy of the cavity plus dislocation loop defect in Fig. 3(b) may be estimated[73] as

$$E_2 = 2\pi R_r^2 \sigma_r + \pi \mu R_d b^2 [\ln(R_d/b) - 1]/2(1-\nu), \tag{6}$$

where R_d is the radius of the dislocation loop, μ is the shear modulus of the host crystal (in terms of the elastic constants,[74] $\mu = C_{44} - H/5$, where $H = 2C_{44} + C_{12} - C_{11}$), b is the Burgers vector of the dislocation, and ν is Poisson's ratio. Clearly, $E_1 > E_2$ for R_u greater than some critical value, R_{uc} or for μ less than a critical value, μ_c. For the case of Si at room temperature, the shear modulus is[70] $\mu(\mathrm{RT}) = 6.81 \times 10^{11}$ erg/cm^3, while[75] $b = 0.384$ nm, and $\nu = 0.215$. Also, for Si(111) surfaces,[25] $\sigma_u = 904$ erg/cm^2. The value of σ_r is not known empirically but can be estimated[25] by noting that the reconstructed surface is about 26% less dense than the unreconstructed surface and is free of dangling bonds. This estimate is $\sigma_r = 613$ erg/cm^2. If we further suppose that the pillar regions discussed in (i) lie entirely within the original cavity, we estimate

$$R_d = R_u, \tag{7}$$

and

$$R_r = (1.0 - 0.26)^{1/2} R_u = 0.86 R_u. \tag{8}$$

Let us further assume that the cavity reconstructs as soon as it attains the minimum extent,[59] $D_c = 6$–8 nm, necessary for reconstruction. Then, taking the minimum empirical value for D_c,

$$R_c = \tfrac{1}{2} D_c = 3 \text{ nm}, \tag{9}$$

one calculates,

$$E_1 = 5.11 \times 10^{-10} \text{ erg}, \tag{10}$$

while

$$E_2 = 2.56 \times 10^{-10} + 2.02 \times 10^{-10} = 4.58 \times 10^{-10} \text{ erg}. \tag{11}$$

Therefore, with Si at room temperature, any cavity that is large enough to reconstruct can do so with sufficient energy to produce the dislocation loop indicated in Figs. 2 and 3. Thus,

$$R_{uc}(\mathrm{Si}) = 0,$$

and (12)

$$\mu_c(\mathrm{Si}) = 8.6 \times 10^{11} \text{ erg/cm}^3.$$

However, as this minimal excess energy is only about 10% of E_1, the formation of the dislocation may be an improbable event in such cases. If the cavity reconstructs without producing a dislocation, the defect will produce little lattice strain and probably would not be detected by TEM unless it becomes decorated with impurities, in which case it would appear as a precipitate.

As one goes to higher temperatures, the temperature variation of μ must be considered. The author has found empirical values of $d\mu/dT$ only for room temperature and below.[76] However, it can be calculated from theories relating the elastic constants to the electronic structure[71] and a knowledge of the temperature dependence of the electronic structure.[77,78] (This theory fits the room-temperature temperature dependence to

about 20%.) This leads to the estimate for Si at its melting point T_m,

$$\mu(\mathrm{Si}, T_m) = 0.8\mu(\mathrm{Si}, \mathrm{RT}) = 6.45\times10^{11}\ \mathrm{erg/cm^3}. \quad (13)$$

Neglecting thermal expansion of b and any temperature variation of σ_u and σ_r, this leads to the estimate that E_1 exceeds E_2 by about 20% for the minimum sized cavity that could reconstruct at T_m.

In the case of GaAs at room temperature, the shear modulus is[70] $\mu = 4.85\times10^{11}$ erg/cm^3, while[79] $\nu = 0.29$ and $b = 0.399$ nm, and[25] $\sigma_u = 812$ erg/cm^3 and $\sigma_r = 495$ erg/cm^3. With $R_u = 3$ nm, the minimum value possible for reconstruction, a calculation as above leads to

$$E_1(\mathrm{GaAs}, \mathrm{RT}, 3\ \mathrm{nm}) = 4.59\times10^{-10}\ \mathrm{erg}, \quad (14)$$

while

$$E_2 = 2.07\times10^{-10} + 1.66\times10^{-10} = 3.73\times10^{-10}\ \mathrm{erg}. \quad (15)$$

Again we conclude that any cavity which can reconstruct would do so with sufficient energy to produce the sort of dislocation loop here hypothesized (Figs. 2 and 3). However, the minimum energy release is only about 19% so that again it is probable that the dislocation loop will not always be formed.

(vi) Finally, we consider the question of the conditions under which one ought to expect the precipitation of vacancies to produce "vacancy-type" dislocations loops in semiconductors. This question is relevant because there are a few observations[80,81] of vacancy-type dislocations in these materials where most dislocations are observed to show interstitial-type lattice bowing in the electron microscope. The important point here would seem to be that reconstruction is a thermally activated process.[41,60,61] It would seem that rewelding should occur without an activation barrier if unreconstructed surfaces (with dangling bonds in compatible orientation) are mechanically forced together by any stress field that happens to be present. If the dislocation is nucleated at too low a temperature, the reconstruction mechanism will not be competitive against rewelding. Although one would have to consider the details of a particular case to make an accurate estimate, a crude assumption, that the critical temperature T_c, dividing the regimes of nucleation of vacancy-type and of interstitial-type dislocation loops is that for which the mean time to reconstruction is 600 sec, leads[41,60] to the estimate that $T_c(\mathrm{Si}) = 390\,^\circ\mathrm{C}$ and that $T_c(\mathrm{GaAs}) = 380\,^\circ\mathrm{C}$.

Once the loop has been nucleated and has started to grow as one type or the other, one should expect it to continue to grow as that same type. In the case of an "interstitial-type" loop, this follows because of the tensile strain field outside the perimeter, where the vacancies would tend to cluster and permit the lattice planes on either side of the extra partial plane to separate further apart. In the case of a "vacancy-type" dislocation, this would follow because the vacancies would tend to cluster on the outside perimeter of the loop, where the atoms are not well bonded (Fig. 1) so that $\Delta H_f(V)$ is small, and would permit the host-lattice planes on each side of the missing partial plane to come together and reweld. Note that in both cases vacancies will be approaching the core of the dislocation predominantly from the outside of the loop because the dislocation is gettering them from the bulk of the crystal.

The distinction just made may serve to resolve the discrepancy between the reports by Kimerling *et al.*[15] and by O'Hara *et al.*[16] that dark line defects (DLD's) in GaAlAs lasers are a convolution of interstitial-type dislocations, and the report by Woolhouse *et al.*[80] that the dislocations, at least in optically degraded material, are in fact of vacancy type. The former two groups studied DLD's which formed about dislocations that were produced during crystal growth and thus were nucleated while the crystal was hot enough for reconstruction to occur in times of order 10 msec. Woolhouse *et al.* studied DLD's which formed about dislocations that were introduced into the sample by scratching its surface at room temperature and causing it to glide by optical excitation. The mean time to reconstruction over the activation barrier at room temperature is calculated to be[41] or order 10^{12} years.

IV. PROPOSED EXPERIMENTS THAT MAY VERIFY THE MECHANISM

Although the mechanism proposed here has the attraction that it would serve to resolve the fundamental question of the nature of deep point and line defects by explaining the general observation of extrinsic stacking faults and "interstitial-type" dislocations without invoking any self-interstitials, and thus contradicting the general conclusion that vacancies are far more numerous, it should be subjected to further scrutiny.

One fairly clear distinction between this mechanism and the alternative that the dislocations are formed by the precipitation of self-interstitials that were incorporated during crystal growth is that the present mechanism implies the presence of voids in the crystal taking up somewhat fewer lattice sites than the initial number of vacancies, i.e., of order 10^{15}–10^{16} per cm^3, while the self-

interstitial mechanism implies there will be many orders of magnitude less void. As was noted in Sec. II, the presence of small (or order 6 nm) voids is difficult to detect[29] by TEM. One could not distinguish the difference in absorbing power from surface effects and noise. The scattering intensity from vacancies and interstitials is the same in the absence of lattice distortions. In either case there would be lattice distortion due to impurities because both types of dislocation would tend to attract impurities[82] by their strain fields. (In fact, the dislocations are almost always observed to be decorated with impurities.[83]) However, the presence of such voids should be detected if one diffuses a radioactive gas, such as ^{3}H or ^{37}Ar or ^{41}Ar or ^{39}Ar, through the sample[84] and measures the radioactivity remaining in the sample. As these gases diffuse rapidly and interstitially, there would be a negligible concentration of these on substitutional lattice sites, but they would tend to be trapped within any voids in the sample.

Other interstitially diffusing impurities, such as Cu or Li, would also be expected to precipitate into any cavities that are present in the interior of the loop as well as around the perimeter. With the self-interstitial mechanism, one would expect to find such precipitates only about the core of the dislocation and not in the body of the loop, which should be perfect material according to that model. Therefore, by determining the number of atoms of Li or of Cu which precipitate at low temperatures on dislocation loops that were previously grown into the sample, such as the swirl defects[85] in Si, and comparing this to the number of sites on the perimeter of the loops and to the number of sites within the loops, one should be able to determine if the impurity is restricted to the dislocation core. It may also be possible to detect the presence of such impurities in the body of the loop by high-resolution electron energy-loss analysis[86] or by x-ray microanalysis.[87]

It should be noted that the absence of Moire fringes in the body of many of these loops is not conclusive evidence that the material in the loop is perfect. It may just as well be that the material is highly disordered, essentially amorphous in that region, or that it consists of pillars of perfect material dispersed between regions of void or of disordered material.

ACKNOWLEDGMENTS

This work was encouraged by John W. Matthews, now deceased, as fine a scientist and a man as the author has ever known. The author has also benefited from discussions with R. A. Ghez, T. S. Kuan, and D. V. Lang. G. R. Woolhouse suggested Fig. 3 and the calculation in Eqs. (5)–(15). This work was supported in part by the Air Force Office of Scientific Research under contract No. F49620-77-C-0005.

[1]J. W. Matthews and J. A. Van Vechten, J. Crystal Growth 35, 343 (1976).
[2]A. U. MacRae, Bull. Amer. Phys. Soc. 22, 306 (1977).
[3]H. Shiraki, in *Semiconductor Silicon 1977*, edited by H. R. Huff and E. Sirtl (Electrochemical Society, Princeton, 1977), pp. 546.
[4]R. B. Fair and J. C. C. Tsai, J. Electrochem. Soc. 124, 1107 (1977).
[5]E. Nes and J. Washburn, J. Appl. Phys. 44, 3682 (1973).
[6]E. Nes, Phys. Status Solidi A 33, K5 (1976).
[7]S. M. Hu, J. Vac. Sci. Technol. 14, 17 (1977).
[8]P. M. Petroff and A. J. R. deKock, J. Cryst. Growth 30, 117 (1975).
[9]A. Seeger, H. Föll, and W. Frank, in *Radiation Effects in Semiconductors 1976*, edited by N. B. Urli and J. W. Corbett, Conf. Ser. No. 31 (Institute of Physics, Bristol, 1977), p. 12.
[10]H. Föll and B.O. Kolbesen, Appl. Phys. 8, 319 (1975); H. Föll, U. Gösele, and B.O. Kolbesen, J. Crystal Growth 40
[11]A. J. R. deKock, in Ref. 3, p. 508.
[12]J. R. Patel, Ref. 3, p. 521.
[13]J. A. Van Vechten, J. Electrochem. Soc. 122, 1556 (1975).
[14]G. R. Woolhouse, IEEE J. Quantum Electron. 11, 556 (1975).
[15]L. C. Kimerling, P. M. Petroff, and H. J. Leamy, Appl. Phys. Lett. 28, 297 (1976).
[16]S. O'Hara, P. W. Hutchinson, and P. S. Dobson, Appl. Phys. Lett. 30, 368 (1977).
[17]G. D Watkins, in *Lattice Defects in Semiconductors 1974*, edited by A. Seeger, Conf. Ser. No. 23 (Institute of Physics, London, 1975), p. 1.
[18]C. Weigel, D. Peak, J. W. Corbett, G. D. Watkins, and R. P. Messmer, Phys. Rev. B 8, 2906 (1973).
[19]J. A. Van Vechten, in Ref. 9, p. 441.
[20]H. C. Casey, M. B. Panish, and L. L. Chang, Phys. Rev. 162, 660 (1967).
[21]J. A. Van Vechten, in Ref. 17, p. 212.
[22]J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B 14, 3551 (1976).
[23]J. C. Phillips and J. A. Van Vechten, Phys. Rev. Lett. 30, 220 (1973).
[24]J. A. Van Vechten, Phys. Rev. B 10, 1482 (1974).
[25]J. A. Van Vechten, J. Electrochem. Soc. 122, 419 (1975).
[26]S. Mader and A. E. Michel, Phys. Status Solidi A 33, 793 (1976) and (private communication).
[27]P. S. Dobson (private communication).
[28]J. Friedel, *Dislocations* (Pergamon, Oxford, 1964), p. 91.
[29]J. M. Cowley, Acta Crystallogr. A 29, 529 and 537 (1973).
[30]W. C. Dash, J. Appl. Phys. 31, 2275 (1960).
[31]V. A. Phillips and W. C. Dash, J. Appl. Phys. 33, 568 (1962).
[32]L. S. Milevskii, Sov. Phys.-Solid State 4, 1792 (1963).
[33]T. Iizuka, J. Appl. Phys. Jpn. 4, 1018 (1966).

[34]R. W. Balluffi, Phys. Status Solidi 31, 443 (1969), especially Fig. 1 of Part 2. Note the correction at the end of the caption to this figure.
[35]J. M. Silcock and W. J. Tunstall, Philos. Mag. 10, 361 (1964).
[36]R. Räty and H. M. Miekk-eja, Philos. Mag. 18, 1105 (1968).
[37]F. Seitz, Phys. Rev. 79, 723 (1950).
[38]L. M. Brown and G. R. Woolhouse, Philos. Mag. 21, 329 (1970).
[39]T. Y. Tan and W. K. Tice, Philos. Mag. 34, 615 (1976).
[40]N. H. Fletcher, J. Crystal Growth 28, 375 (1975).
[41]J. A. Van Vechten, J. Vac. Sci. Technol. 14, 992 (1977), especially pp. 994–995.
[42]A. A. Chernov and S. I. Budurov, Kristallografiya 9, 388 (1964) [Sov. Phys.-Crystallogr. 9, 309 (1965)].
[43]A. A. Chernov and S. I. Budurov, Kristallografiya 9, 466 (1964) [Sov. Phys.-Crystallogr. 9, 388 (1965)].
[44]K. A. Jackson, Philos. Mag. 7, 1117 (1962).
[45]T. L. Davis and J. P. Hirth, J. Appl. Phys. 37, 2112 (1966).
[46]J. J. Lander and J. Morrison, J. Appl. Phys. 34, 1403 (1963).
[47]J. J. Lander, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, Oxford, 1965), Vol. 2, p. 26.
[48]F. Jona, IBM J. Res. Dev. 9, 375 (1965).
[49]P. Mark and W. R. Bottoms, in Ref. 47, Vol. 6, 1971, p. 17.
[50]F. Bäuerle, W. Mönch, and M. Henzler, J. Appl. Phys 43, 3917 (1972).
[51]W. Mönch, in *Advances in Solid State Physics* (Pergamon-Vieweg, Braunschweig, 1973), Vol. 13, p. 241.
[52]J. C. Phillips, Surf. Sci. 40, 459 (1973).
[53]K. C. Pandey (unpublished).
[54]H. Brooks, *Impurities and Imperfections* (American Society for Metals, Cleveland, 1955), p. 84.
[55]N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).
[56]J. Schmit and A. A. Lucas, Solid State Commun. 11, 415 (1972).
[57]J. A. Van Vechten, Phys. Rev. B 11, 3910 (1975).
[58]J. A. Appelbaum and D. R. Hamann, Phys. Rev. B 6, 2166 (1972).
[59]J. E. Rowe, S. B. Christman, and H. Ibach, Phys. Rev. Lett. 34, 874 and 1298(E) (1975).
[60]J. A. Van Vechten, Appl. Phys. Lett. 26, 593 (1975).
[61]J. A. Van Vechten, J. Crystal Growth 38, 139 (1977).
[62]H. C. Abbink, R. M. Broudy, and G. P. McCarthy, J. Appl. Phys. 39, 4673 (1968).
[63]L. J. Cheng, J. C. Corelli, J. W. Corbett, and G. D. Watkins, Phys. Rev. 152, 761 (1966).
[64]C. A. Ammerlaan and G. D. Watkins, Phys. Rev. B 5, 3988 (1972).
[65]G. Saada and J. Washburn, J. Phys. Soc. Jpn. 18 Suppl. 1, 43 (1963).
[66]J. A. Van Vechten, Phys. Rev. B 7, 1479 (1973) especially p. 1491.
[67]J. Friedel, in Ref. 28, p. 74.
[68]H. Brooks, in Ref. 54, p. 1.
[69]P. N. Keating, Phys. Rev. 145, 637 and 149, 674 (1966).
[70]R. M. Martin, Phys. Rev. B 1, 4005 (1970).
[71]J. A. Van Vechten, Phys. Rev. B 10, 4222 (1974).
[72]F. A. Kröger, Ann. Rev. Mat. Sci. 7, 449 (1977).
[73]J. Friedel, in Ref. 28, p. 22.
[74]J. P. Hirth and J. Lothe, *Theory of Dislocations* (McGraw-Hill, New York, 1968), p. 404.
[75]See Ref. 74, p. 762 (Note the error in the values of H and of μ quoted for Si in this table).
[76]H. J. McSkimin, W. L. Bond, E. Buelher, and G. K. Teal, Phys. Rev. 83, 1080 (1951).
[77]C. D. Thurmond, J. Electrochem.Soc. 122, 1133 (1975).
[78]J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B 14, 3539 (1976).
[79]N. A. Goryunova, *The Chemistry of Diamond-like Semiconductors* (MIT, Cambridge, Mass., 1965), p. 99.
[80]G. R. Woolhouse (unpublished).
[81]G. H. Olsen (private communication); H. Kressel, C. J. Nuese, and G. H. Olsen, J. Appl. Phys. (to be published).
[82]J. Friedel, in Ref. 28, Chap. 13.
[83]J. P. Hirth and J. Lothe, in Ref. 75, p. 462.
[84]A. Van Wieringen and N. Warmoltz, Physica (Utr.) 22, 849 (1956).
[85]A. J. R. deKock, Philips Res. Rep. Suppl. 1, 1 (1973).
[86]J. Silcox, Scanning Electron Microsc. 1 393 (1977).
[87]H. Koike, T. Namae, T. Watabe, and A. Miksjiri, Jpn. Electron Opt. Lab. News 10, 2 (1973).