JOURNAL OF MATERIALS SCIENCE 10 (1975) 1636–1641

Interstitial condensation in n^+ GaAs

P. W. HUTCHINSON, P. S. DOBSON
Department of Physical Metallurgy and Science of Materials, University of Birmingham, Birmingham, UK

Transmission electron microscopy of annealed tellurium-doped gallium arsenide has shown that a high constitutional interstitial defect population is present in n^+ as-grown material. The point defects precipitate into the form of perfect interstitial dislocation loops when annealed above 380° C. The equivalent point defect concentration within the loops remains constant during isochronal and isothermal anneals and is dependent on the tellurium level. Copper diffusion is also found to influence the point defect concentration and copper may be the element responsible for the formation of the precipitates often associated with the large dislocation loops.

1. Introduction

Faulted dislocation loops have been observed [1, 2] in as-grown crystals of gallium arsenide containing a high concentration ($> 10^{18}$ cm^{-3}) of tellurium. The faults are of extrinsic character and it was concluded that they consist of a layer of gallium telluride inserted between the $\{111\}$ planes of the gallium arsenide lattice. Although little change was observed in the distribution of these faulted defects when the material was annealed in the temperature range 400 to 1000° C, it was found that prismatic dislocation loops, which were not present in the as-grown crystal, nucleated and grew during the anneal. This paper is concerned with the origin of these prismatic loops.

The prismatic dislocation loops [2, 3] were unfaulted, had a Burgers vector of type $(a/2)\langle 110\rangle$ and were of interstitial character. It was not possible to determine from contrast analysis whether the prismatic loops were formed from the condensation of native interstitials, i.e. arsenic and gallium, or from impurities and contaminants such as tellurium and copper. However, it was demonstrated [2] that when thin foil specimens were irradiated with 1 MeV electrons at 450° C the prismatic loops grew whereas no change was observed for the faulted loops. Since the gallium and arsenic interstitials created during the irradiation were readily adsorbed by the prismatic loops it was concluded that the prismatic loops were originally formed from native interstitials. The fact that the faulted loops did not adsorb the interstitials created by irradiation indicates that they are composed of a different chemical species, i.e. gallium telluride to the prismatic loops.

Laister and Jenkins [3] showed that the prismatic loop distribution depended on the annealing temperature but the total loop area per unit volume of material was found to increase with increasing tellurium concentration. Different loop distributions were observed in Czochralski pulled crystals than in crystals prepared by gradient freeze methods and Laister and Jenkins concluded that the point defects responsible for loop formation were introduced into the crystal during crystal growth.They also suggested that loop formation was strongly influenced by copper contamination possibly through its role in dissociating the native point defects. Laister and Jenkins [3] discussed these effects in terms of vacancies since they had concluded from contrast analysis that the loops were of vacancy type. However, since it has now been established that the prismatic loops are of interstitial type the purpose of this paper is to re-examine these phenomena in terms of the precipitation of interstitials.

2. Experimental

The gallium arsenide specimens used in this work were all Czochralski pulled $\langle 001\rangle$ single crystals containing tellurium, selenium or zinc. The dopant concentrations quoted refer to the electrically active concentrations and are, therefore, minimum values of the total dopant concentrations. Slices, 0.5 mm thick, were cut

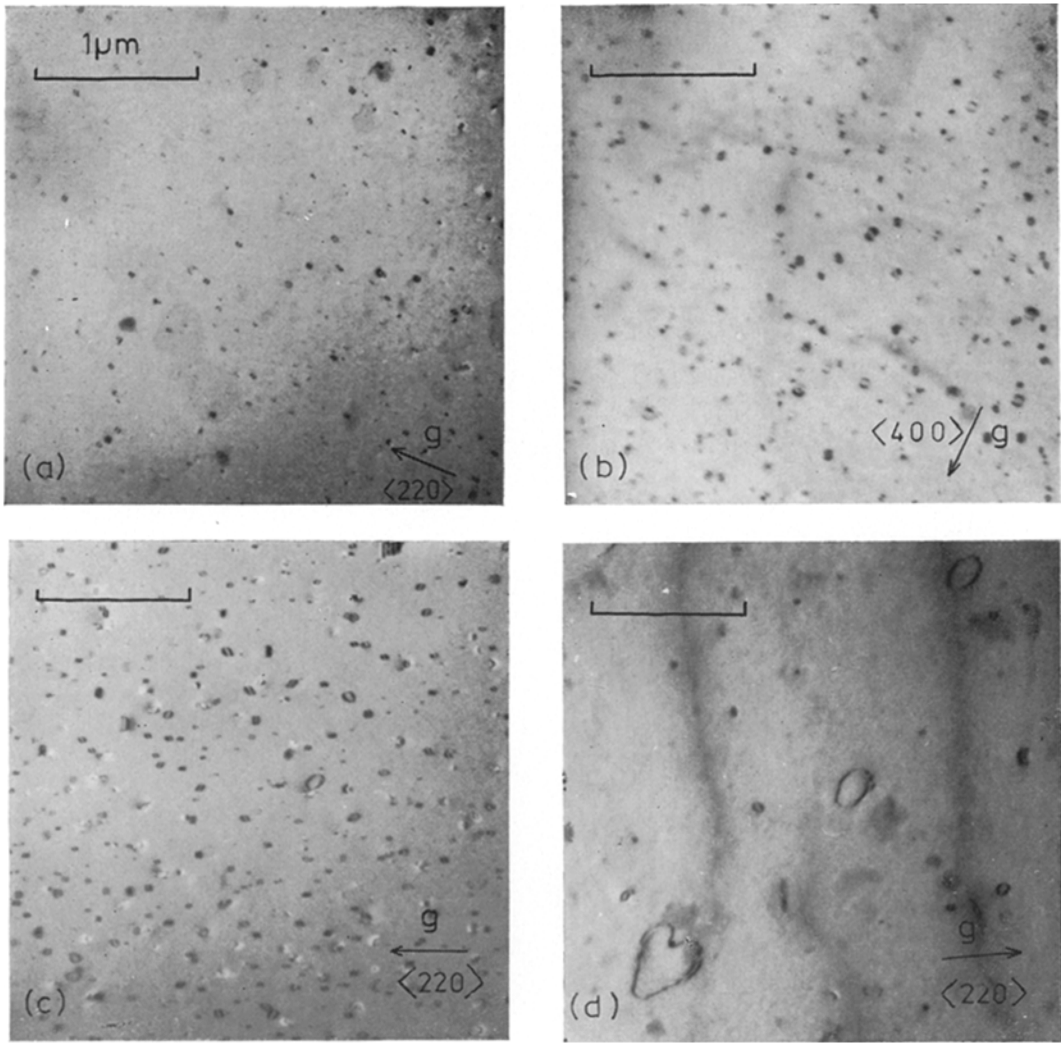

Figure 1 Typical bright-field electron micrographs showing the variation in loop distribution with annealing temperature in a (001) GaAs specimen containing 8.4×10^{18} Te atoms cm^{-3} annealed for 4 h. (a) 380° C, (b) 580° C, (c) 780° C, (d) 980° C.

from the crystals perpendicular to the growth axis and 3 mm diameter discs were cut from these, sealed in small evacuated vitrosil capsules and annealed in the temperature range 400 to 1000°C. In some cases a few milligrams of elemental arsenic or copper were included in the capsules before annealing. Foils suitable for examination in an AEI EM6G or Philips EM300 electron microscope were then prepared using the method of Buiocchi [4].

3. Results

3.1. Effect of annealing treatment

The effect of the annealing temperature was studied by annealing specimens containing the same tellurium concentration (8.4×10^{18} cm^{-3}) for a constant time at various temperatures. A typical set of micrographs is shown in Fig. 1 and the results are summarized in Table I. These results are in general agreement with those obtained by Laister and Jenkins [3] and show that the loop size increases and the loop density decreases with increasing annealing temperature. No loops were observed for annealing temperatures below 380°C and above 1000°C although isolated dislocation lines which may result from large loops intersecting the foil surfaces were occasionally seen for annealing temperatures

TABLE I Isochronal annealing results for Te-doped GaAs containing 8.4 × 10^{18} Te cm^{-3}. 4 h anneal

Anneal temperature (°C)	Average loop density (cm^{-3})	Average loop size (Å)	Approximate loop area per unit volume (cm^{-1})	Equivalent interstitial concentration (cm^{-3})*	Comments
980	$\leqslant 2 \times 10^{12}$	3000	1410	2.4×10^{18}	{110} loops only
780	1.2×10^{13}	500	230	2.5×10^{18}	{110} loops
	8×10^{13}	$\leqslant 500$	1400		{111} loops
580	1.2×10^{14}	350	1380	2×10^{18}	mainly {111}
380	1.8×10^{14}	300	1200	1.8×10^{18}	all {111} loops

*Rough estimates assuming the loops contain a double layer of arsenic and gallium interstitials.

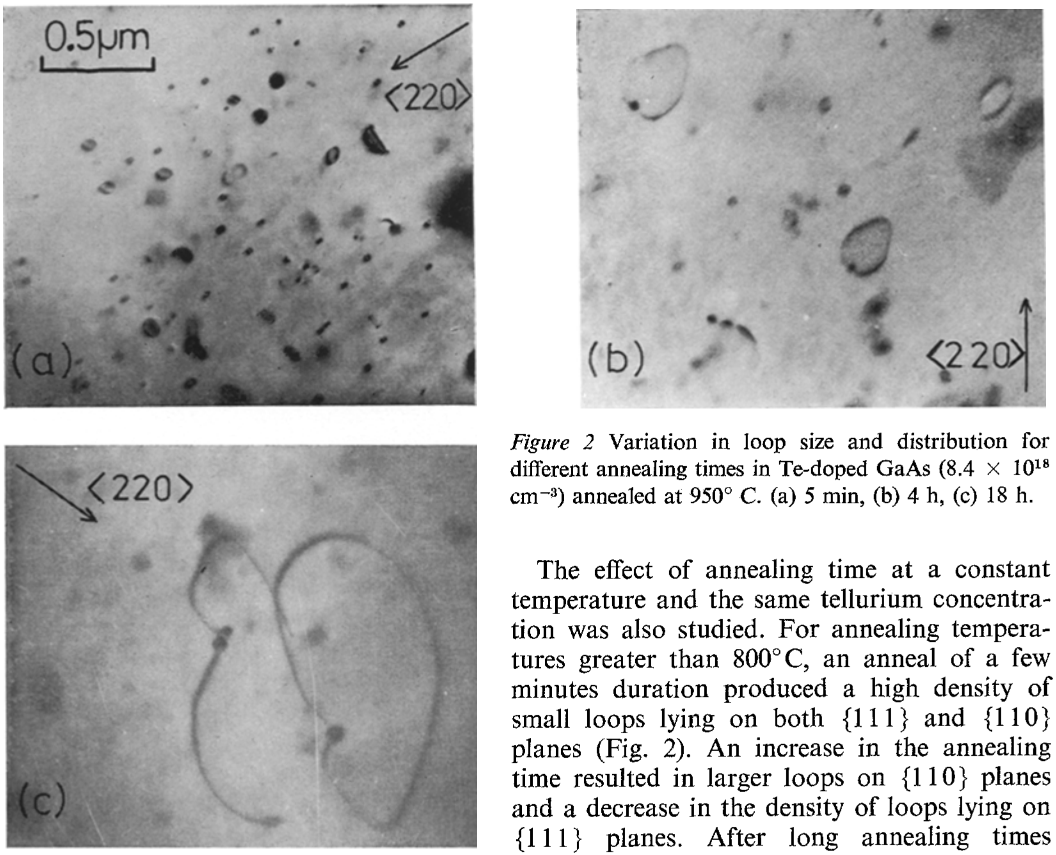

Figure 2 Variation in loop size and distribution for different annealing times in Te-doped GaAs (8.4 × 10^{18} cm^{-3}) annealed at 950° C. (a) 5 min, (b) 4 h, (c) 18 h.

above 1000°C. For annealing temperatures below 800°C, small loops lying on {111} planes predominated whereas for temperatures in the range 800 to 1000°C, loops lying on {110} planes were predominant. The total loop area per unit volume was constant, within experimental error, for all annealing temperatures. The large loops observed after the higher temperature anneals ($T \gtrsim 800$°C) contained discrete precipitates (Fig. 1d) and were often heart or parallelogram shaped.

The effect of annealing time at a constant temperature and the same tellurium concentration was also studied. For annealing temperatures greater than 800°C, an anneal of a few minutes duration produced a high density of small loops lying on both {111} and {110} planes (Fig. 2). An increase in the annealing time resulted in larger loops on {110} planes and a decrease in the density of loops lying on {111} planes. After long annealing times (~ 50 h) no loops were observed to lie on {111} planes but the loops lying on {110} planes had increased in size and decreased in density. The total loop area per unit volume remained approximately constant for all annealing times. These coarsening effects were less obvious in specimens annealed at temperatures below 800°C and loops lying on {111} planes were still present after annealing for 100 h at 400°C.

Some specimens were given identical annealing treatments in the range 800 to 1000° C but were cooled at different rates by either rapidly quenching into water or by slow cooling within the furnace. No significant differences in the loop distribution was observed indicating that the loops are formed during the anneal and are unaffected by the rate of cooling.

The rate of cooling was found to have a significant effect when the annealing temperature was in excess of 1000° C. Under these conditions loops were not normally observed after rapid cooling but it was found that loops were present in specimens which had been annealed at 1150° C and furnace cooled. Although no loops were observed in specimens which had been annealed at 1150° C and rapidly quenched, loops were produced on subsequent annealing at a lower temperature. An anneal at 1150° C was found to cause the disappearance of loops since specimens which had been annealed at temperatures below 1000° C and then annealed at 1150° C and rapidly cooled were free of loops. These results indicate that the crystal is close to equilibrium at 1150° C but is supersaturatedwith the defects responsible for loop formation at temperatures below 1000° C.

3.2. Effect of doping impurity

The effect of the tellurium concentration on the loop distribution was studied by annealing specimens of different tellurium concentrations at the same temperature and time. It was found that over a tellurium concentration range of 4×10^{17} to 8.5×10^{18} cm^{-3} the density and size of the loops decreased with decreasing tellurium concentration while no loops were observed in specimens containing less than $\sim 1 \times 10^{18}$ cm^{-3} of tellurium. This effect can be seen in Fig. 3 which shows micrographs taken of annealed specimens containing 8.4×10^{18} and 4.5×10^{18} cm^{-3} of tellurium. The total loop area per unit volume was estimated at about 1400 cm^{-1} for the most heavily doped specimen and < 100 cm^{-1} for the more lightly doped specimen. On the assumptions that a loop is composed of a double layer of gallium and arsenic interstitials these figures correspond to a total interstitial concentration of about 2×10^{18} and $< 1 \times 10^{17}$ cm^{-3} respectively.

Dislocation loops were also observed in annealed gallium arsenide crystals containing 4×10^{18} atom cm^{-3} of selenium although the total loop area per unit volume was less than in a specimen doped with the same nominal concentration of tellurium. No loops were observed in annealed p-type gallium arsenide containing 1×10^{19} atoms cm^{-3} of zinc or in annealed undoped gallium arsenide containing less than 10^{16} carriers cm^{-3}.

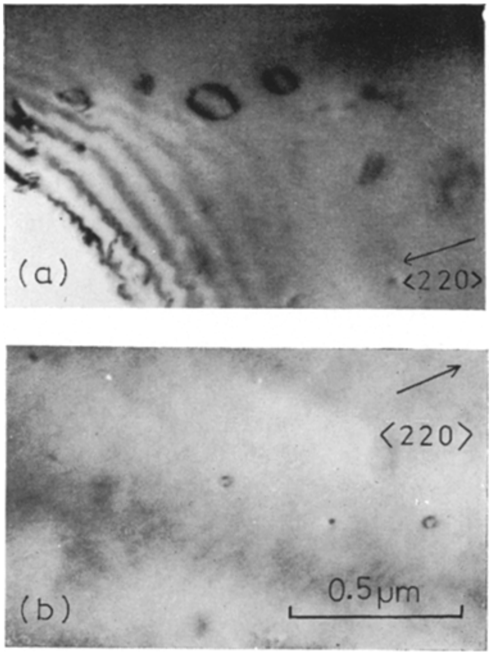

Figure 3 Dependence of loop distribution on the tellurium concentration in specimens given identical heat-treatments (4 h at 870° C). (a) 8.4×10^{18} Te atoms cm^{-3}, (b) 4.5×10^{18} Te atoms cm^{-3}.

3.3. Effect of annealing atmosphere

Some specimens were annealed at the same temperature in atmospheres of different arsenic partial pressures. No significant difference in the loop distribution was observed between specimens annealed in a vacuum of 10^{-4} Torr and in a saturated arsenic atmosphere. The effect of any surface reactions was also studied by comparing the loop distributions in foils adjacent to the specimen surface with that in foils prepared by thinning from both surfaces of the 500 µm thick specimens. Again no detectable changes in the loop distribution were observed.

Some specimens were annealed in an evacuated capsule containing about 50 mg Cu. Fig. 4 shows a micrograph of a specimen containing 6×10^{18} atoms cm^{-3} of tellurium annealed for 5 h at 985° C. Under these conditions large parallelogram-shaped loops were observed and each loop contained one precipitate at one corner of the parallelogram. These loops are also of interstitial type [2]. In other regions of the same

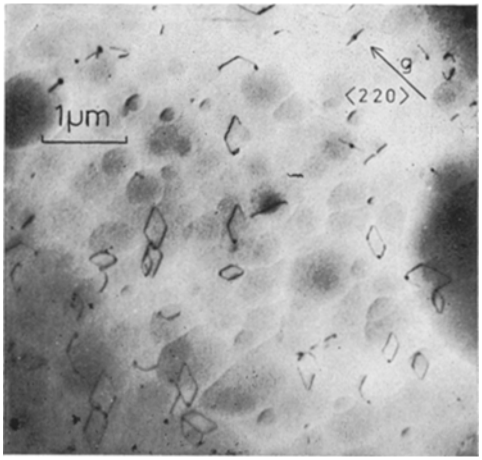

Figure 4 Typical area containing a high density of parallelogram-shaped loops in Te-doped GaAs annealed in the presence of copper.

specimen, isolated circular and heart-shaped loops were occasionally observed among the parallelogram loops.

It was also found that the total loop area per unit volume was greater in specimens annealed in the presence of copper than in specimens of the same tellurium concentrated annealed in vacuum. For example the loops shown in Fig. 4 correspond to an interstitial concentration of approximately 3.0×10^{18} cm^{-3} whereas an interstitial concentration of 6×10^{17} cm^{-3} was obtained for an identical specimen annealed in the absence of copper.

4. Discussion

The experimental results show that prismatic dislocation loops of interstitial character form when n^{+} gallium arsenide is annealed in the temperature range 400 to 1000° C. It is concluded from the structure of the loops that equal numbers of gallium and arsenic interstitials are involved and that these interstitials are not created as a result of any surface reactions since the total loop area is independent of depth in the specimen and the arsenic partial pressure in the annealing atmosphere. The fact that similar values of the total loop areas were obtained from specimens of the same doping concentration subjected to various isochronal and isothermal annealing treatments also supports this conclusion.

The interstitial atoms required for loop formation can either be present in the as-received crystal in the form of a quenched-in interstitial supersaturation or may be created during the anneal to accommodate some other precipitation process [5]. This second possibility will first be discussed. Since many of the large loops contain a precipitate it is possible that large lattice strains are created during the growth of the precipitate which are relieved by the removal of material which then condenses to form the interstitial loops. It is impossible to distinguish these two possibilities from the observations alone but this mechanism appears unlikely from a consideration of the kinetics of the process. If it is assumed that the precipitate is formed first, then it follows from the observation that the total loop area increases with increasing tellurium concentration, that the precipitate is formed from excess tellurium. The diffusion of tellurium in gallium arsenide at 1000° C has been measured [6] to be 10^{-3} cm^2 sec and if it is assumed that $D = \exp(-Q/kT)$ then an estimate of the diffusion coefficient at lower temperatures can be determined. The distance travelled by a tellurium atom during an anneal is $\sim \surd(Dt)$ which is equal to $\sim 10^{-2}$ Å for a 1 h anneal at 400° C. It thus appears unlikely that any significant migration of tellurium can occur at the lower temperature at which loop formation occurs and thus it is concluded that tellurium precipitation is not necessary for loop formation. If the particles are formed by the precipitation of some fast diffusing species such as copper, loop formation would be expected to occur in undoped material and the strong dependence on tellurium concentration would not be observed. Furthermore no evidence of precipitation on the loops in material annealed at less than 800° C was detected using the weak beam technique and, therefore, it is concluded that the interstitial loops are not formed as a result of impurity precipitation but rather that they are created by the condensation of an excess concentration of quenched-in interstitials.

This conclusion that the interstitials are quenched-in is at first sight somewhat surprising since the crystals are slow cooled from the melt but can be shown to be quite feasible by the following analysis. The mean square distance travelled by an interstitial $\langle\lambda^2\rangle$ is given by

$$\langle\lambda^2\rangle = nb^2 \qquad (1)$$

where n is the number of jumps made by the interstitial during cooling and b is the jump distance. The number of jumps made by the interstitial per second is

$$\nu_0 \exp(-E_m/kT) \tag{2}$$

where ν_0 is the lattice vibration frequency ($\sim 10^{13}$ sec^{-1}) and E_m is the interstitial migration energy. Thus the mean square distance travelled by an interstitial when the crystal is cooled from a temperature T_0 to T is in time t given by

$$\langle\lambda^2\rangle = b\nu_0 \int_0^t \exp(-E_m/kT)\mathrm{d}t \cdot \tag{3}$$

If we make the rough approximation for the sake of mathematical simplicity that the crystal cools according to

$$T = \frac{T_0}{1 + t/\tau} \tag{4}$$

where τ is the time required for T to reach $T_0/2$, then Equation 3 can be integrated to give

$$\langle\lambda^2\rangle = \frac{b^2\nu_0 kT_0\tau}{E_m} \{\exp(-E_m/kT_0) - \exp(-E_m/kT)\}$$

$$\sim \frac{b^2\nu_0 kT_0\tau}{E_m} \exp(-E_m/kT_0) \cdot \tag{5}$$

The dislocation density in the crystal is $\sim 10^4$ cm^{-2} and a large proportion of the interstitials will be quenched in if

$$\langle\lambda^2\rangle < 2.5 \times 10^{-5}\ \text{cm}^2 . \tag{6}$$

Thus if we take $T_0 \sim 1200°$ C and $\tau \sim 10^3$ sec a quenched-in supersaturation of interstitials will occur if $E_m > 1.3$ eV.

The concentration of quenched-in interstitials increases rapidly with increasing tellurium concentration above a threshold of $\sim 10^{18}$ cm^{-3} and it is interesting to note that this value is of similar magnitude to the intrinsic carrier concentration at or near the growth temperature [7]. If the interstitials act as acceptors with an acceptor level E_A then the equilibrium concentration of interstitials is given by

$$c = c^*[(1 + 2n_D/n_I)\exp(E_F{}^I - E_A)/kT]$$

where c^* is the concentration of neutral interstitials, $E_F{}^I$ is the Fermi level in intrinsic gallium arsenide and n_D and n_I are the electron concentrations in doped and undoped material respectively. Thus the experimental observations that the interstitial concentration increases with increasing tellurium concentration can be accounted for on the basis of a large concentration of negatively charged interstitials in n^+ material.

The interstitial loops were only observed after annealing the as-received material which is somewhat surprising since the crystal underwent a similar heat-treatment during cooling from the melt. It is suggested, therefore, that the absence of interstitial loops after crystal growth is due to a lack of suitable nucleating agent which subsequently enters the crystal. It is interesting to note that loops have also been observed in n^+ substrates after epitaxial deposition and are presumably created as a result of the high temperatures employed for epitaxial deposition [8]. The nature of the nucleating agent is not known but one possibility is that a fast diffusing species such as copper is involved which may also be responsible for the precipitates observed on some of the large loops. The presence of copper also increases the total loop area presumably since it diffuses as an interstitial and then transfers to a substitutional lattice site thereby creating a native interstitial which can be absorbed by the prismatic loops. The presence of copper alone is insufficient to create loops since no loops were observed in copper diffused intrinsic material.

Acknowledgement

The authors acknowledge financial support from the Ministry of Defence (DCVD).

References

1. D. LAISTER and G. M. JENKINS, *J. Mater. Sci.* **3** (1968) 584.
2. P. W. HUTCHINSON and P. S. DOBSON, *Phil. Mag.* **30** (1974) 65.
3. D. LAISTER and G. M. JENKINS, *ibid* **23** (1971) 1077.
4. C. J. BUIOCCHI, *J. Appl. Phys.* **38** (1967) 1980.
5. J. M. SILCOCK and W. J. TUNSTALL, *Phil. Mag.* **10** (1964) 361.
6. J. F. OSBORNE, K. G. HEINEN and H. RISER, previously unpublished from H. C. CASEY, in "Atomic Diffusion in Semiconductors" edited by D. Shaw (Plenum Press, London, 1973).
7. R. N. HALL and J. H. RALETTE, *J. Appl. Phys.* **35** (1964) 379.
8. P. W. HUTCHINSON, unpublished.

Received 11 November 1974 and accepted 3 February 1975.