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Direct Observation of Dislocation Loops in Arsenic-Doped Germanium

The presence of dislocation loops in germanium resulting from condensed vacancies has been assumed[1,2] to explain various deformation, diffusion, and etching phenomena. Booker and Stickler[3] have recently shown that such dislocation loops can be observed in thin foils of *n*-type germanium by transmission electron microscopy. The loops were produced in arsenic-doped germanium containing 10^{16} atoms/cc by quenching bulk material from 850°C, thinning by chemical polishing to make foil approximately 1500 A thick, and annealing the foil in the high-intensity electron beam. The loops, which grew with continued annealing, eventually transformed into discs, and Booker and Stickler explained the results by suggesting the formation of clusters consisting of vacancies and impurity atoms. According to their model, the growing clusters, upon reaching a critical size, collapse to form loops. The loops can then absorb more impurity atoms and ultimately transform into platelike particles.

The purpose of this Letter is to present further evidence that dislocation loops can be produced easily in *n*-type germanium and that the impurity-vacancy interaction is an important consideration in their formation. It is also demonstrated that loop formation does occur during the annealing of bulk germanium as distinct from the thin foil annealing in Ref. 3.

During a study of the precipitation kinetics of an arsenic phase in germanium heavily doped with arsenic,[4] it was found that the kinetic data could not be explained readily in terms of simple diffusion-controlled precipitation on pre-existing nuclei as described by Zener[5] and Ham.[6] It was desirable, therefore, to examine the precipitating phase in order to establish a mechanism for the process and to understand the kinetic behavior. Single-crystal germanium doped with approximately 5×10^{19} arsenic atoms/cc was solution heat-treated at 875°C for $\frac{1}{2}$ hour and rapidly quenched in water. Electrical resistivity and Hall measurements on the material indicated that this treatment was adequate to achieve complete solution, since longer heating times gave no additional change in electrical properties. Samples were then annealed at various temperatures and times below the solution temperature, and the precipitation was followed by measuring the increase in electrical resistivity with time. Similar treatments were given to both high-purity germanium and germanium doped with 5×10^{19} gallium atoms/cc. Electron transmission samples, approximately 1500 A thick, were prepared by an electrolytic jet-etching technique[7] and examined in a Phillips EM100 electron microscope. The electron beam intensity was not high enough to cause any apparent changes in sample structure by localizing heating.

Dislocation loops were not observed in either the high-purity germanium or gallium-doped germanium. The samples were structureless and, as pointed out by Booker and Stickler, one would not expect to see edge dislocations, for example, in electron transmission because a dislocation density of 10^5 per cm^2 would correspond to only one dislocation/m^2 at 30,000× magnification. This was verified by plastically deforming germanium to contain approximately 10^6 dislocations/cm^2; it was difficult to find evidence of dislocations in transmission microscopy even at this density.

Figures 1(a) and 1(b) are transmission photographs of a solution-treated and quenched arsenic-doped sample. The dark circular areas[8] in Fig. 1(b) were observed infrequently but they have also been seen by Booker and Stickler.

Figure 2 is a transmission photograph of a sample which has been completely precipitated at 550°C. The density of loops is about 10^8/cm^2 and they appear to be oriented on $\{110\}$ planes. The density of blackening of the loops is not consistent with merely diffraction contrast effects due to orientation and is probably due to precipitation at the loops. This idea is substantiated by the work of G. H. Schwuttke,[9] who reports that X-ray transmission photographs reveal arsenic precipitation on dislocation lines.

Upon re-solution and requenching a previously precipitated sample from 875°C, the loops were found to disappear completely. Simultaneously the initial sample resistivity was restored, indicating that the arsenic was redissolved into an electrically active state.

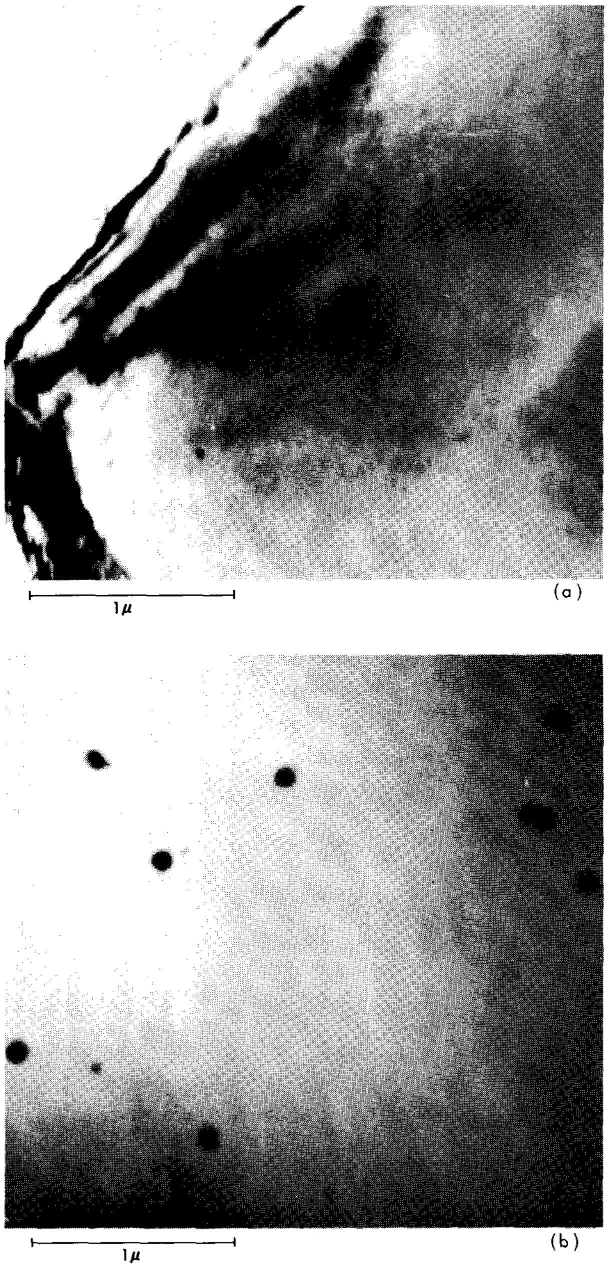

Figure 1 **Arsenic-doped germanium (5 × 10^{19}/cc quenched from 875°C).**

(a) *Typical structureless sample showing no evidence of collapsed vacancy loops.*

(b) *Dark spots infrequently observed and attributed to vacancy-impurity interaction.*

Our data support the mechanism proposed for loop formation in arsenic-doped germanium, and we can further postulate why loops are not observed in high-purity nor in gallium-doped germanium.

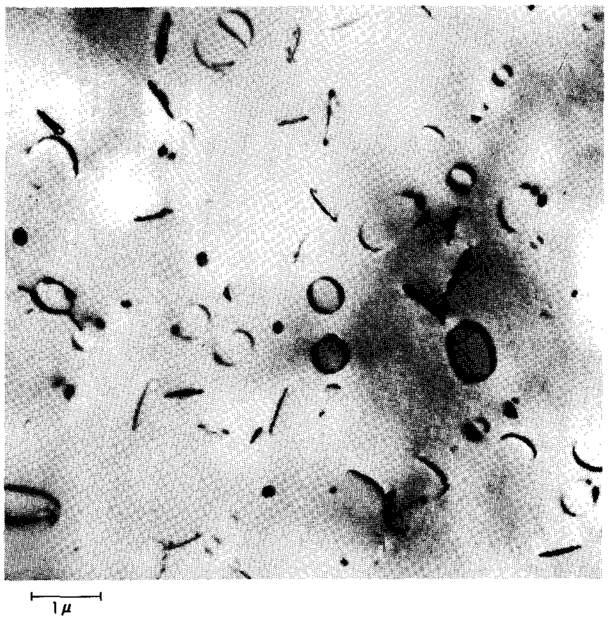

Figure 2 **Arsenic-doped germanium quenched from 875°C and annealed for 7 hrs at 550°C.**

Collapsed dislocation loops are well defined. The plane of the photograph represents a (111) *crystallographic plane.*

The numbers of vacancies in thermal equilibrium at the solution temperature are estimated to be 3 × 10^{14}/cc and 4 × 10^{15}/cc for high-purity germanium and germanium containing 5 × 10^{19} arsenic atoms/cc, respectively. These quantities are not sufficient to form clusters large enough to collapse into observable loops upon quenching as is the case, for example, in aluminum.[10] The vacancy loops observed in arsenic-doped germanium are hence attributed, not to thermal vacancies, but rather to those released by the precipitating arsenic at the annealing temperature. Their number is about four to five orders of magnitude larger than the number of thermal vacancies.

During the annealing treatment, although the electrical resistivity increases immediately, loops appear only after a given time, which is temperature dependent. In this initial period, it is concluded that arsenic leaves solid solution and releases vacancies which cluster and grow. When they collapse into dislocation loops, the rate of precipitation increases, which suggests that the loops then serve as growth sites for further precipitation. Although the arsenic concentration in Booker and Stickler's germanium was three orders of magnitude lower than that used in this study, the difference would probably be reflected in loop density and size.

Since gallium-doped germanium is not susceptible to precipitation effects, the mechanism for producing vacancies cannot occur and hence dislocation loops are not observed.

Acknowledgments

We wish to thank C. J. Lent for growing the arsenic-doped germanium, B. K. Bischoff for performing the heat treatments and S. Mader and H. Widmer for helpful discussions.

References and footnotes

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Received May 1, 1962