Thermal Effects on Lifetime of Minority Carriers in Germanium

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Earlier work has shown that germanium may be heated to elevated temperatures (~875°C) without significant change in its room temperature resistivity, provided special care is taken to prevent chemical contamination. Such precautions were not sufficient, however, to prevent a drastic decrease in the minority carrier lifetime.

In the present work it is shown that if, in addition to cleanliness, special precautions are taken to avoid the introduction of strains or plastic flow in the germanium crystal, minority carrier lifetimes in excess of 100 microseconds can be maintained after such heat treatments.

WHEN germanium is heated to 500°C or higher, changes usually occur in the resistivity.[1] It has been shown[2] that these changes are due to the entrance of atomic copper into the crystal lattice during the heat treatment. These changes in resistivity may be prevented[3] by precleaning the germanium crystal surface and heating in an atmosphere which is relatively free of volatile impurities. However, these procedures are not sufficient to prevent large changes in the room temperature lifetime of minority carriers.[4]

Recent experiments have shown that to maintain high lifetime, not only must the level of chemical contamination be further reduced, but also care must be taken to prevent damage to the crystal lattice during the heat treatment. Methods have been developed so that it is now possible to heat germanium to elevated temperatures (~875°C) for several minutes, retaining original resistivity and, in addition, a room temperature lifetime of several hundred microseconds. In the experiments reported on here, lifetime was measured by the method of Haynes and Hornbeck.[5]

If electrons and holes were to recombine only by a radiative annihilation process, then the lifetime would be about one second at room temperature.[6] Observed lifetimes, being much smaller than this, indicate the presence of recombination centers. Three types of recombination centers are known: (1) chemical impurities;[7] (2) dislocations introduced into crystals by plastic deformation;[8] and (3) crystal imperfections[9] such as vacancies or interstitial atoms whose high-temperature equilibrium concentration may be "frozen in" if the crystal is rapidly quenched[4] after heating.

The following procedures were applied in the successful attempt to prevent the introduction of these three respective types of centers.

1. To remove chemical contamination, the germanium surface was cleaned by methods already described.[4] The heating was performed in a large stainless steel vacuum system with a residual pressure of about 2×10^{-5} mm Hg. Germanium specimens were heated by clamping them between chemically cleaned molybdenum electrodes and passing current through the specimen.

2. To avoid plastic deformation during heating, one electrode was made as flexible and as lightweight as possible to minimize the stress exerted on the sample. The sample was suspended in a vertical position between this electrode and a fixed upper electrode. With this heating arrangement germanium rods with cross section 0.1 in.×0.1 in. (or larger) were heated to high temperature (~875°C) for several minutes. They retained their original resistivity and had a lifetime in excess of 100 μsec. Rods of smaller cross section, e.g., 0.05 in.×0.1 in., could not be heated successfully in this way due, presumably, to the deformation caused by the small residual stress exerted by the electrodes. However, such rods could be heated on a flat horizontal molybdenum strip which was held between similar electrodes and maintained at 935°C for 10 minutes. The rods, heated in this way, retained their original room temperature lifetime ($\tau\sim150$ μsec).

3. To avoid quenching effects, the samples were cooled slowly (approximately 100°C/min). However, if the rods were rapidly cooled by shutting off the power after the heat cycle, the lifetime was lowered. For example, a rod, rapidly cooled in this way after heating on the molybdenum strip as described above, had the lifetime reduced from 150 μsec to 50 μsec.

The results presented here may be applied in the design of a heating system in which germanium may be heated to elevated temperature for extended times without impairing resistivity, and in addition, maintaining a high lifetime.

[1] H. C. Theuerer and J. H. Scaff, Trans. Am. Inst. Mining Met. Engrs. **191**, 59 (1951).
[2] C. S. Fuller and J. D. Struthers, Phys. Rev. **87**, 526 (1952); W. P. Slichter and E. D. Kolb, Phys. Rev. **87**, 527 (1952).
[3] R. A. Logan, Phys. Rev. **91**, 757 (1953).
[4] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953).
[5] Navon, Bray, and Fan, Proc. Inst. Radio Engrs. **40**, 1342 (1952); R. A. Logan, Phys. Rev. **91**, 757 (1953).
[6] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), Chap. 3.
[7] Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 853 (1953).
[8] Pearson, Read, and Morin, Phys. Rev. **93**, 666 (1954).
[9] G. L. Pearson (private communication); also, see reference 5, p. 347.