M. I. Nathan
S. H. Moll*

Electron Beam Microanalysis of Germanium Tunnel Diodes

The purpose of this Letter is to describe the results of electron beam microanalysis of impurities in germanium tunnel diodes. The apparent possibilities and limits of applicability for tunnel diode technology will be discussed.

The properties of a *p-n* junction are determined by the concentrations and distributions of donor and acceptor impurities in the junction. Tunnel diodes are normally made by alloying a highly soluble impurity, sometimes held in a carrier metal, into a semiconductor crystal heavily doped with an impurity of the opposite type. A schematic diagram of a cross-section of a tunnel diode is shown in Fig. 1. The *p-n* junction is at the interface between the regrown region and the substrate. The impurity concentrations are of the order of one part in 10^3, and certain dimensions are sometimes as small as a few microns. In order to determine the concentrations of impurities, it is necessary to resort to indirect techniques such as capacitance measurements on the junctions and Hall effect and resistivity measurements on crystals before the junctions are fabricated. Such techniques, however, leave many questions unanswered: (1) What is the concentration of impurities in the regrown region? (2) Is the impurity concentration uniform over the interface? (3) Are there any changes in impurity concentration in the substrate during alloying?

A technique which can help answer these questions is electron beam microanalysis. This is a method for quantitatively analyzing the chemical composition of small regions of solid specimens. A finely focused beam (< 2 microns in diameter) of high energy ($\sim$30 kv) electrons is focused on a metallographically prepared cross-section of the sample. This excites the X-ray spectra of the atoms in the sample. An X-ray spectrometer is used to observe the characteristic emission lines. From measurement of the intensity of the lines, the concentration of a particular impurity element can be determined.

The microanalysis measurements were carried out at Advanced Metals Research Corporation. The application of this technique to semiconductor problems has been described by Wittry, Axelrod and McCaldin.[1] The depth of penetration of the electron beam is $\sim$1 micron in germanium. The beam size is found to be between 1 and 2 microns, from visual observation of scintillation of an NaCl crystal. It was observed that the apparent spot size and positional stability of the beam were improved if the sample were first coated with a thin ($\sim$50 A) conducting film, either aluminum or copper, by vapor deposition. This presumably helped to inhibit any charge build-up on the surface of the specimen, which was insulating epoxy except for the diode.

All diodes were made by a fast alloying process on a hot stage, i.e., the alloying time was one second or less. The diodes were mounted in epoxy resin with the plane of the junction making an angle of approximately 20° with the surface of the microsection, as shown in Fig. 1. In order to determine the absolute value of the impurity concentration, a sample of germanium containing a concentration of the impurity determined by Hall effect measurement was placed in the microsection cup. In the case of gallium and arsenic this could be compared with the concentration measured by using gallium arsenide as a standard. The two methods of determination agreed to within the statistical error for both gallium and arsenic.

The results of runs on the gallium concentration and the arsenic concentration in a diode made by alloying a 1% gallium-in-indium dot in germanium containing 3.6×10^{19} cm^{-3} arsenic atoms are shown in Figs. 2 and 3. In Fig. 1 the x direction, which makes an angle of 45° with the interface, shows a typical path for the electron microanalysis run. The diode had a current density of approximately 200 amp/cm^2, which is typical for diodes made on substrates of this arsenic concentration.[2] Since the gallium and arsenic runs were not taken simultaneously, abscissas cannot be compared directly. Moreover, the interface between the regrown region and the substrate was not directly visible during the runs because of the metal coating and polishing. However, visual estimates made by comparison of photographs taken with the boundary

* Advanced Metals Research Corporation, Somerville, Massachusetts.

visible and those taken immediately after the run place the boundary at $x = 105\mu$ in Fig. 2 and $x = 110\mu$ in Fig. 3. The gallium run is one of three runs on the same diode; the arsenic is one of two. Similar results were obtained on the other runs. It is seen that a gallium concentration of 8×10^{19} cm^{-3} gives a counting rate of about 43% above background (zero gallium concentration in germanium). It is assumed that there is no gallium in the substrate. For reasonable counting times a counting rate of 5% above background is set as the limit of detectability. Hence the limit of detectability for gallium is 10^{19} cm^{-3}. For arsenic it is about 1.5×10^{19} cm^{-3}.

There are several interesting features of Figs. 2 and 3. First the gallium concentration in the regrown region is considerably below the solid solubility[3] of gallium in germanium (5×10^{20} cm^{-3}). This was also found in runs on another similarly constructed diode. These latter measurements, however, were complicated by the fact that the width of the regrown region was only about five microns.

Estimation of the gallium concentration at the interface which probably coincides with the *p-n* junction is difficult, since the gallium concentration increases rapidly with distance into the regrown region. The concentration is certainly less than 4×10^{19} cm^{-3} and probably around 2×10^{19} cm^{-3}. The gallium concentration at the junction is comparable with the arsenic concentration in the substrate (3.6×10^{19} cm^{-3}); therefore, both impurity concentrations are important in determining the properties of the junction.

The arsenic concentration drops to about the limit of detectability as the interface is crossed (1.5×10^{19} cm^{-3}) and then increases to a value greater than the

Figure 1 **A schematic diagram of a tunnel diode.** *The plane of the microsection is shown in the upper drawing.*

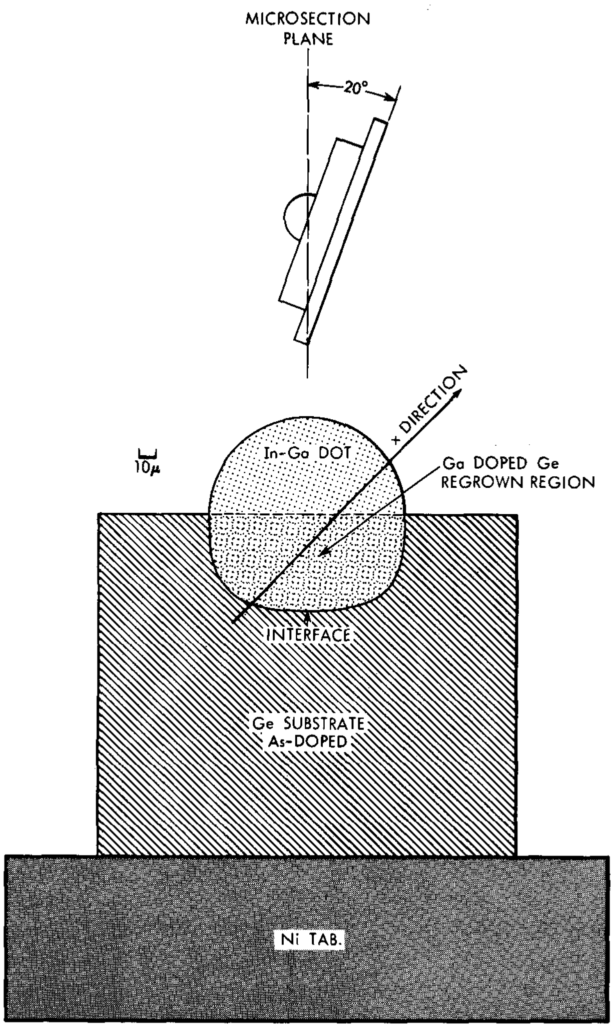
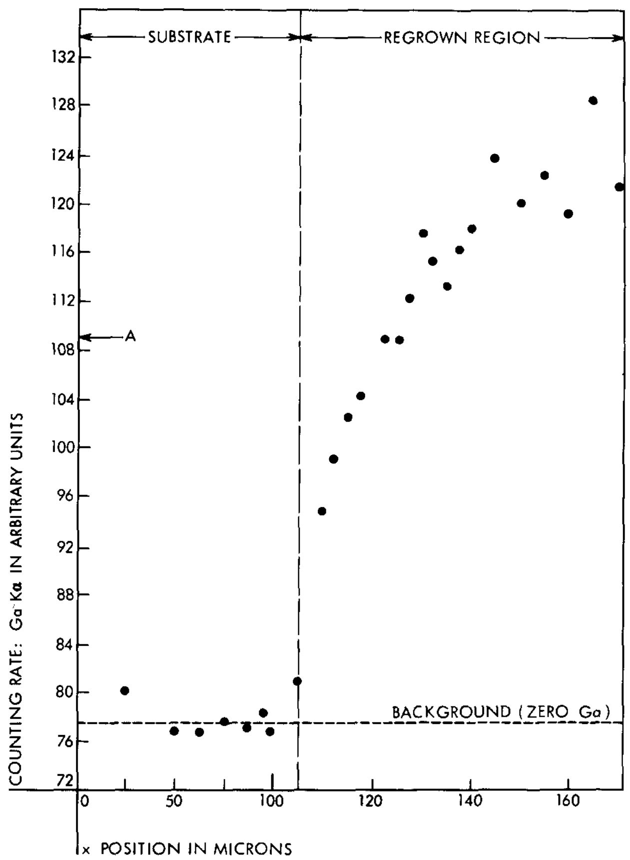


Figure 2 **Gallium electron beam microanalysis on a tunnel diode made by alloying a 1% gallium in indium dot into an arsenic-doped substrate containing 3.6×10^{19} cm^{-3} arsenic atoms.** *Note the scale change at 100 microns. Point "A" is the counting rate for 8×10^{19} cm^{-3} Ga-doped Ge.*



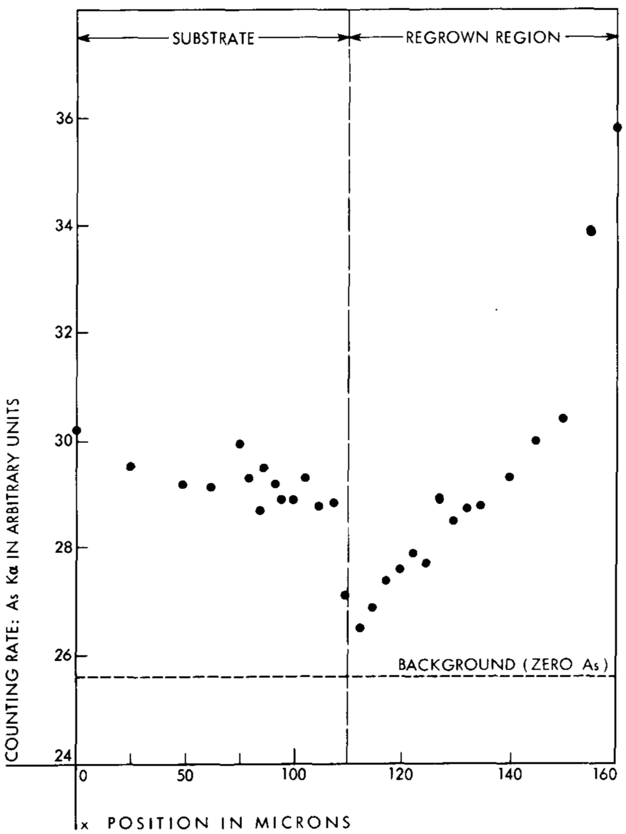


Figure 3 **Arsenic run in the same diode as Fig. 2.** *Note scale change at 100 microns.*

concentration in the substrate, at the boundary between the regrown region and the indium dot. Apparently a large amount of the arsenic dissolved during the alloying process is rejected to the regrown region during solidification. This is in agreement with other measurements.[2,4]

Gallium runs were also made on a diode which had been fabricated by alloying pure gallium into arsenic-doped germanium. A concentration of approximately 8×10^{20} cm^{-3} gallium was found in the regrown region. The regrown region on this diode was not wide enough to measure the gradients of gallium concentration.

Runs for indium and aluminum in germanium were also made. The indium run was made on the regrown region from a dot consisting of 1% gallium in indium. The density of indium was found to be below the limit of detectability, which was approximately 10^{20} cm^{-3}. This was to be expected since the solubility of indium in germanium[3] is only about 4×10^{19} cm^{-3}. Aluminum runs were made on the regrown region from a pure aluminum dot. The limit of detectability is about 5×10^{19} cm^{-3}. The concentration of aluminum decreased sharply with distance from the substrate interface. Beyond 10 microns from the interface, the concentration was below the limit of detectability. Because of this sharp gradient it is almost impossible to get any quantitative information. A very rough estimate of the concentration of the aluminum at the substrate interface is 5×10^{20} cm^{-3}.

Conclusion

Electron microanalysis has been used to measure aluminum, arsenic, gallium and indium in germanium. It is most useful for gallium, which has a high solubility in germanium. The present work indicates that the gallium concentration in the regrown region is small enough to be important in determining the width of the space charge region in tunnel diodes. The apparent resolution of the instrument makes it useful for measuring in regrown regions.

The technique is less useful for arsenic in germanium, since it is not quite as sensitive as for gallium. It appears that it is of little practical use for the determination of indium or aluminum concentrations in germanium encountered in tunnel diode technology.

Acknowledgment

The suggestion by F. Dill to apply electron beam microanalysis to the study of tunnel diodes is gratefully acknowledged.

References

1. See D. B. Wittry, J. M. Axelrod and J. O. McCaldin, page 87 in *Properties of Elemental and Compound Semiconductors*, Edited by H. C. Gatos, *Metallurgical Society Conferences*, Vol. 5, Interscience Publishers, Inc., New York, 1960.
2. C. Lanza, 1962, unpublished work.
3. F. A. Trumbore, *Bell System Tech. J.* **39**, 205 (1960).
4. See F. A. Trumbore, page 15 in *Metallurgy of Elemental and Compound Semiconductors*, Edited by R. O. Grubel, *Metallurgical Society Conferences*, Vol. 12, Interscience Publishers, Inc., New York, 1961.

Received April 23, 1962