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Approved

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This bulletin discusses the spreading of indium over germanium surfaces in the alloy process. The specific problem of spreading of unrestricted indium droplets in the fabrication of high-frequency transistors is discussed in detail. The occurrence of two classes of spreading is noted, and other observations are made which lead to characterization of the spreading characteristics as dependent on a crystal property. A controlled experiment is described in which alloy spreading is compared on two crystals having widely different edge-dislocation densities. The conclusion that the presence of edge-dislocation sites serves to limit alloy spreading of indium is developed. A mechanism of faster alloy penetration through the (111) crystal surfaces in the presence of an edge dislocation is postulated to explain the observed effects. Finally, the practical application of the developed postulate to alloy-junction transistor fabrication is discussed briefly.

Introduction

This bulletin discusses the role of edge dislocations[1] in the control of the geometry of indium-germanium alloy transistors. Although in the experiments described, unrestricted indium droplets were alloyed onto germanium (111) surfaces, the results are general, and the conclusions can be extended to explain the spreading behavior of indium over germanium (111) surfaces in the conventional alloy process, whether or not restrictive jigs are used. The discussion assumes planar junctions, which may be made by the method described in LB-990[2].

Alloy-Junction Transistor Geometry

The functional geometry of a transistor is described by the junction areas and the spacing 'W' between the junctions. Fig. 1 shows a diagrammatic cross section of an alloy-junction transistor. Junction spacing is determined by the germanium-wafer thickness and the indium penetration. The junction area is the spread area of the indium. The indium penetration depends on the mass and the spread area of the indium, and on the alloying temperature. The extent of spreading is important, therefore, because it influences not only the junction area but the junction spacing as well.

With the use of the indium-germanium phase diagram, the penetration of the alloy front has been calculated[3], showing its relation to the size of the indium sphere used, the alloying temperature, and the extent of indium spreading over the germanium surface. When any two of these parameters are held constant, the effect of variations in the third on penetration can easily be determined.

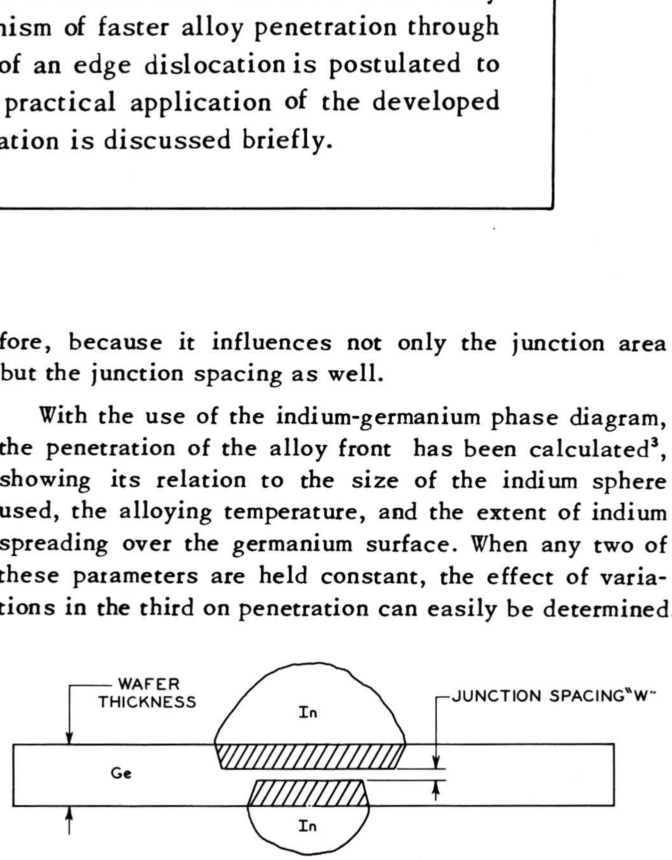

Fig. 1 – Idealized cross section of indium-germanium alloy transistor.

As an example, consider the following specific case- A 0.010-inch indium sphere is alloyed to a germanium (111) surface at a temperature of 550 degrees centigrade in such a manner that the spread diameter of the indium is 0.014 inch. Calculations given in RB-23 indicate that the design-center indium penetration is 0.000485 inch. Fig. 2a shows the variation of penetration with alloy temperature. A change of 5 degrees from the design-center alloy temperature of 550 degrees Centigrade causes a difference in penetration of 0.000024 inch.

[1] 'Dislocations in Germanium,' S. G. Ellis, *Jour. Applied Physics* 26, (Sept. 1955) p. 1140.

[2] LB-990 *Uniform Planar Alloy Junctions for Germanium Transistors,* by C. W. Mueller and N. H. Ditrick.

[3] RB-23 *Calculations of Alloying Depth of Indium by Germanium,* by L. Pensak.

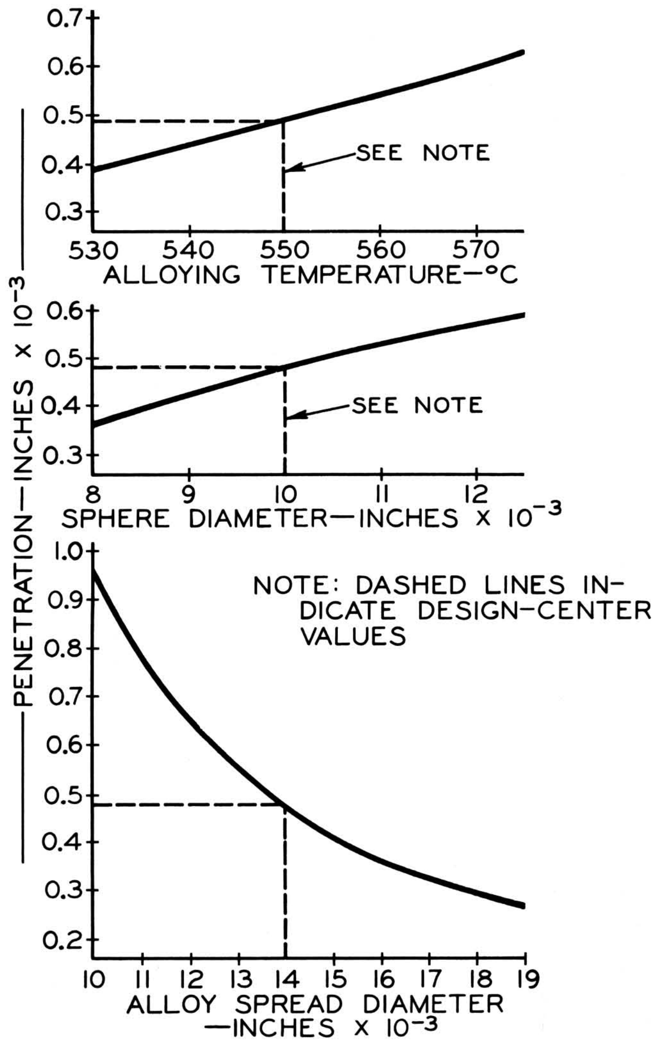

Fig. 2 – Variations of indium alloy penetration with changes in alloying temperature, sphere diameter and alloy spread diameter.

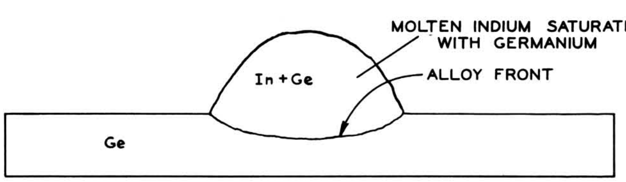

Fig. 3 – Idealized cross section of an unrestricted indium droplet on germanium at the alloying temperature.

Fig. 2b shows the variation of penetration with sphere diameter. A 0.001-inch variation in sphere diameter causes a variation in penetration of about 0.00005 inch. Variations in spreading also cause penetration changes, as shown in Fig. 2c. A 0.001-inch variation in spreading causes a change in penetration of about 0.00007 inch at the design center; this difference becomes greater if the sphere does not spread to a diameter near the design-center value of 0.014 inch. Such variations may be tolerated. Alloying temperatures can be controlled within 5 degrees, and indium spheres can be reproduced with a diameter variation of less than 0.001 inch. Larger variations often occur in spreading, however, causing corresponding changes in indium penetration. In the past, the physical factors controlling the spreading of indium over a germanium surface have not been clearly understood, and their control has proved difficult.

The Spreading of Indium on Germanium

A clean piece of indium placed on a germanium surface and heated to a temperature above 155 degrees Centigrade melts and tends to assume a spherical shape. Because the presence of oxides on the surface of the indium is detrimental to the wetting of the germanium surface, the alloying operation is normally performed in a reducing atmosphere. As the temperature is raised, the indium spreads over the germanium surface, dissolving bulk germanium as it spreads. At any given temperature, the spreading seems to cease when the indium has become saturated with dissolved germanium. Consequently, the indium does not continue to spread without limit over the germanium surface, but reaches a terminal condition in which the indium approximates a spherical cap in external appearance. This cap lies over a saucer-like depression in the germanium surface as shown in Fig. 3. This simple procedure produces the characteristic curved junction. If a chemical flux is used to spread the indium spheres at a low temperature, with subsequent flux removal and alloying at higher temperature, a planar junction such as that shown in Fig. 1 is formed.[2]

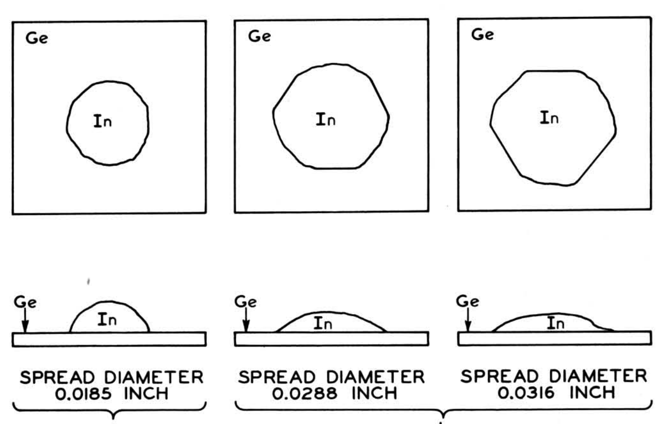

Fig. 4 – Typical samples from spreading experiments.

Although the spread diameters might be expected to exhibit a random distribution in the processes outlined above, experiments prior to the present work showed a much different behavior. In transistors made using the LB-990 process,[2] two classes of spreading were noted.

In the first class, which included about 80 percent of the samples, spread diameters were constant within the accuracy of the measuring equipment. When 0.015 inch spheres were used, the final spread diameter was very close to 0.018 inch, as shown in Fig. 4a. In the second class, which contained the remaining 20 percent of the sample, much more spreading was noted, and diameters were of the order of 0.030 inch. Although the periphery of the alloyed indium was universally circular in the first class, limitation of spreading by (111) planes meeting the surface was predominant in the second class, as shown in Fig. 4b.

Mechanical restrictions, such as the oxide layer formed by alloying in an oxidizing atmosphere, were used in an attempt to restrict excessive spreading. As in the previous case, however, most of the units did not spread during alloying beyond their diameter after the soldering process. The remaining units, which again included about 20 percent of the total number, spread by undercutting the germanium surface, as shown in Fig. 5. This effect indicated that variations in surface tension alone could not explain the excessive spreading; its extent showed that powerful forces were involved.

Edge Dislocations and Spreading

During these early experiments, the edge-dislocation density of the crystal used was not controlled, but was known to average about eight or ten thousand per square centimeter. Large variations of the etch-pit density across the face of a given crystal wafer were noted. Through improvement of crystal growing techniques, it became possible to grow crystals virtually free of edge dislocations. Such crystals were then considered to be of superior quality, and spreading experiments were repeated using low-dislocation-density samples (less than 1000 per square centimeter). Two classes of spread diameter were exhibited, as before, but this time the excessively spread units were more numerous.

In order to show that the observed effects were not caused by variations in processing, a controlled experiment was performed in which spreading was compared on high-dislocation-density (greater than 5000 per square centimeter) and low-dislocation-density (less than 300 per square centimeter) crystals. Each sample wafer was carefully oriented so that the surface was within one degree of a (111) plane. Indium spheres having diameters of 0.010 ± 0.0005 inch were soldered to the wafer surfaces with flux, and soldered spread diameters were measured after flux removal. At this point the diameters were identical within 0.001 inch.

The soldered units were then alloyed in a hydrogen atmosphere at heating and cooling rates of 20 degrees Centigrade per minute. The peak alloying temperature was 550 degrees Centigrade, and the units were held at this temperature for three minutes. Measurement of the post-alloy spread diameters gave positive evidence that the extent of spreading was greater for low-dislocation-density crystals than for high-dislocation-density crystals. Fig. 6 shows the distribution of spread diameters for the two crystals. In each case, two classes of spreading may be distinguished. A small number of units using high-dislocation crystals spread to the diameter exhibited by the majority of the units using low-dislocation crystals.

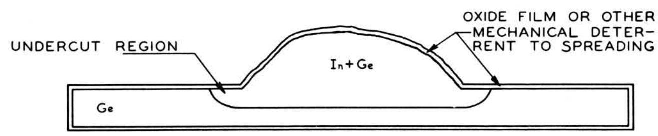

Fig. 5 – Cross section showing tendency of indium to undercut mechanical barriers to spreading.

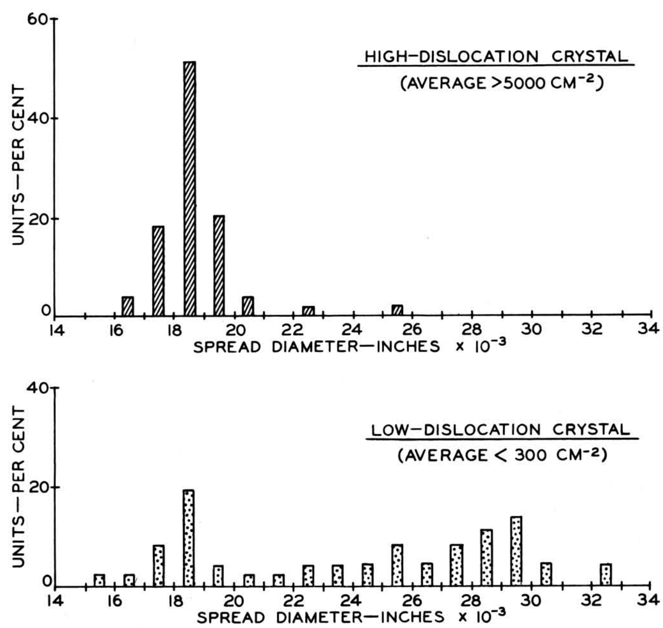

Fig. 6 – Distribution plots of spread diameters on high dislocation crystal and on low dislocation crystal.

Further evidence served to complete the picture. With refined experimental techniques, it was shown in RB-77[4] that a single edge dislocation meeting the germanium surface under an alloying indium pellet would effectively limit spreading. Indium pellets alloyed onto dislocation-free areas of the crystal surface spread excessively. Experiments have indicated the possibility of using dislocation free germanium with special alloying

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[4]RB-77 *Alloying of Indium to Germanium,* by J. I. Pankove.

techniques.[5,6] Whether or not such techniques are practical for the manufacture of transistors remains to be proved.

The experimental evidence leaves no doubt as to the limitation of indium spreading during alloying by the presence of edge dislocations. The mechanism of the effect may be postulated by considering the crystallographic structure of a germanium (111) surface. This crystallographic plane is formed of atoms bonded together in such a way that three bonds must be broken to remove a single atom. Once an atom is broken loose, leaving a defect in the surface, lateral attack is possible, and the (111) surface layer may be 'peeled' off by breaking only one bond for each atom to be separated from the layer below it. Hence, lateral dissolution proceeds more rapidly than penetration of the alloy front in the alloy attack on a perfect (111) plane, and continued spreading results.

If, however, an edge dislocation site meets the (111) surface in the alloy region, it provides ready access to successive (111) layers. When these natural surface defects are present, the attacking indium can readily pass from layer to layer of atoms, and penetration proceeds more rapidly than lateral dissolution. Alloying on (111) surfaces thus involves a competition between penetration and lateral spreading in a dynamic process, and penetration is favored by the presence of edge dislocations.

It is evident that edge dislocations may be used to control alloy spreading by assuring that the indium pellet is located over an edge dislocation. The practical use of this technique requires that a higher dislocation density be used for a smaller alloyed junction area to insure that each area will lie over at least one dislocation. This problem is complicated by the fact that the distribution of dislocations over a wafer surface is not perfectly random. The defects tend to segregate into small-angle grain boundaries, leaving areas of low dislocation density adjacent to high-dislocation-density regions. This tendency increases at higher average dislocation densities, so that the control of the spreading of small indium spheres is by no means perfect. The principle has been successfully applied, however, to the control of a manufacturing process for production of high-frequency alloy-junction transistors.

[5]RB-85 *The Dissolution of Germanium by Molten Indium,* by B. Goldstein.

[6]RB-72 *Alloying Properties of Germanium Free of Edge Dislocations,* by C. W. Mueller.

Conclusions

The following conclusions may be drawn from this study:

1. Edge dislocations meeting germanium (111) surfaces serve to control the spreading of indium in an equilibrium alloying process by providing a ready path for the dissolution of successive (111) atomic layers.
2. If a dislocation is not present at an alloying site, mechanical barriers are relatively ineffective because the indium spreads laterally by undercutting the barrier.
3. Since the distribution of dislocation sites in a crystal is random, a higher average dislocation density must be used with small alloy areas than with larger areas to provide the same degree of spreading control in each case.

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