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SESSION ON MATERIALS—II

GERMANIUM AND SILICON

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(Lecture delivered at the INTERNATIONAL CONVENTION ON TRANSISTORS AND ASSOCIATED SEMICONDUCTOR DEVICES, *21st May,* 1959.)

It is particularly fitting that the first lecture in this session should be devoted to germanium and silicon. Without these two elements and in the absence of the vast amount of basic research and technological development which have been applied to them there would be no transistor, no talk of a revolution in electronics and no convention such as this. Naturally such basic materials attract a lot of attention both technically and financially. I therefore propose to simplify my talk to the proposition that there are few, if any, problems relating to germanium and silicon the solutions to which do not lie in our own hands.

When in the decade 1915–1925 the thermionic valve was taking the place of the earliest type of semiconductor diode (cat's whisker), there was no basic semiconductor theory and no appreciation of the importance of crystal imperfections and impurities. Germanium and silicon did not play any significant part. Silicon first came substantially into the picture with the advent of radar and the birth of modern microwave techniques. Torrey and Whitmer[1] have given an almost classical account of the early stages of this work. With the discovery of the transistor in 1948 reinforcements reached the semiconductor field in the shape of money and brain-power. In particular one might stress the importance of the change-over about this time to mono-crystals. It looked for a while as if the reduction of the problem to regular crystals of the diamond structure with four valencies per atom so simplified theory that technological problems must be solved rapidly. The zone-refining and zone-levelling techniques of Pfann promised to provide easy methods of removing unwanted impurities and distributing desirable ones. We began to talk in terms of the ideal crystal.

About this time we began to become too obsessed with 'cylindrical objects'—rods, etc.—and apt to forget that we were really interested in the crystal characteristics of thin wafers. Between the rod and the wafer much may happen. According

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to some very recent reports from the United States we may eventually produce monocrystalline wafers without recourse to rods as intermediate products.

Occasionally there were rumours that germanium might become scarce, that silicon was proving to be difficult to control and that it might be desirable to investigate certain compound materials whose ingredients were plentiful and cheap. Many people, however, pointed out that we should suffer from inferior mobilities, lower energy gaps, etc., and that the problem of coping with stoichiometric balance would greatly add to our difficulties. In the main, however, we preferred to search for additional germanium in flue dust and to tackle seriously the problem of purifying and controlling silicon.

At that time many people imagined that we were going to obtain ideal germanium and silicon by taking out all significant impurities, and obtaining intrinsic crystals, which we would modify by inserting the desired significant impurities to adjust conductivity, and so on. We explained certain anomalies in this idealistic picture as being due to 'thermium' and 'deathnium'. We had still to examine the complications of further types of impurities, insoluble as well as soluble, compounds (carbides, nitrides) as well as elements and gases as well as solids, with their powerful effects on crystal structure, lifetime and conductivity. Dislocations and etch-pit counts were still mysteries to the technologist. The effects of plastic deformation were still relatively unknown. We had still to experience practically the problem of surface effect and the ability of silicon to pick up undesirable impurities.

In the lecture I shall consider these complications with perhaps as a text the suggestion that the complications become more complex because we are not able so far to agree on a quantitative description or specification of the material we need for transistors and diodes.

Germanium may be used in many cases in preference to silicon because, despite its inferior energy gap, inferior thermal

parameters, more critical surface, etc., it is easier to control and process. Statistically at the moment it would appear that germanium controls the bulk of the transistor field and silicon the bulk of the diode or rectifier field. There are recent signs, however, that silicon may wrest a considerable portion of the transistor field from germanium.

It must be remembered that every time undesirable impurities such as oxygen, copper or iron are encountered they are found in concentrations from say 10^{17} atoms per cubic centimetre down to whatever is the limit of the method of test. The term 'pure germanium' or 'pure silicon' is therefore relative in the context of the limitations of the measurement.

In considering the quantitative specification aspect it must first be accepted that not much assistance will be given by non-electrical methods of trace analysis. Even if expensive radio-activation techniques are employed, giving an accuracy level of 1 foreign atom per 10^{10} or 10^{11} atoms of silicon, there still remain at this level concentrations of impurity atoms of the order of 10^{12} or 10^{11} atoms per cubic centimetre. These can be quite potent concentrations and one could desire even more sensitive means of tests which are not dependent on electrical tests.

Several of the papers presented at the Convention refer to the need to control the oxygen content of silicon. By infra-red methods the oxygen content of silicon cannot be measured much below 10^{16} atoms per cubic centimetre. This is sensitive enough to detect oxygen in crystals pulled from crucibles where values in excess of 10^{17} atoms per cubic centimetre are normal, but if non-crucible-growing methods are used and precautions are taken to keep the partial pressure of oxygen in the ambient atmosphere low (<1 mm), control cannot be checked accurately. Other methods of measuring oxygen, e.g. that based on the kinetics of precipitation of lithium in silicon, give perhaps one order of improvement. Yet (as can be seen in Fig. 1) the removal of an
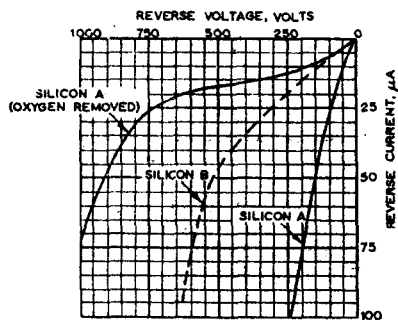
Fig. 1.—Effect of removal of oxygen on behaviour of silicon as a diode material.

indeterminate amount of oxygen may profoundly affect the important reverse-current/voltage characteristics of silicon diodes.

It would be useful again to have more sensitive tests and to be able to determine precisely the level of oxygen concentration, especially in the presence of other impurities, e.g. aluminium,[2] which are dangerous from the points of view of causing thermal conversion (i.e. growth of donor population density), reduced turnover voltage, etc.

The problem is present also in the case of germanium,[3] where concentrations of 10^{16} atoms per cubic centimetre can be detected, with a strong probability of active oxygen atoms acting as double donors.[4]

Turning from such brief examples of relative impotency in the analytical field, many users of silicon are trying to evaluate

the material in terms of the reverse-voltage distribution in sufficiently large production batches of diodes. Fig. 1 has indicated that a good silicon if grown into a crystal in a way which permits adsorption of oxygen may appear to be inferior. In addition, there are other possible errors associated with the processing of the device. In particular one must note that in large batches the uniformity of the crystal must be considered and also that it is extremely difficult to standardize surfaces. If there is considerable variation of surface from device to device the spread of the breakdown voltage will also vary greatly. It must be remembered also that reverse-voltage testing is not necessarily a criterion of silicon quality for transistor manufacture.

Intermediate between trace analysis and evaluation of the end-product comes the more classical method of evaluation by tests covering resistivity, lifetime, dislocation density, etc.

Two important points emerge at the outset. First, although there have been local attempts, e.g. in Great Britain, to standardize methods of test, there is as yet no international standard, and comparison of results is often made doubtful by known or unknown variation of test apparatus and procedures. Secondly, such tests can only be taken on monocrystals, and therefore the quality of the basic material may be masked by the shortcomings of the crystal-growing method. Reference has already been made to the introduction of oxygen by growing silicon crystals in crucible or by failing to reduce the partial pressure of oxygen to a sufficiently low value in the ambient 'inert' atmosphere of a non-crucible grower, or by growing in leaky vacuum.

The crystal-growing procedure also plays a prominent part in producing non-uniformity, longitudinally and radially, in the crystal. In (pulled) germanium crystals there is often a tenfold increase in etch-pit density from the top to the bottom and a variation across a diameter of between 5 and 10 to 1.

Similarly there is normally an excessive variation of resistivity longitudinally and radially. This is undesirable but particularly so if the object of the test is to check impurity content. Non-uniformity of resistivity indicates non-uniformity of distribution of impurities.

Measurement of resistivity alone is no guide to impurity concentration, compensation, etc. Much more elaborate tests, e.g. Hall effect at low temperatures, are necessary. This leads to a dilemma for the supplier of material who may have to supply polycrystalline rods; wishes to check his purification process continuously and rapidly; and is aware that the transformation from polycrystal to monocrystal is fraught with danger of changes which lead to impairment of quality.

Fig. 2 shows an attempt to meet this problem, in so far as boron level in silicon is concerned and as an indication of the efficient working of a silane plant, by measuring the resistivity of polycrystalline or monocrystalline silicon over a range of temperatures and comparing the results against the theoretical curves for pure silicon with various concentrations of boron. In one case (10^3 ohm-cm) the agreement is such that conclusions on the absence of substantial compensation can be legitimately drawn. In other cases (higher resistivity) the situation is obscure.

Lifetime measurements present an even more difficult problem. Although the photoconductive-decay method is that most commonly used for both silicon and germanium, other methods are also employed and again there is no standardization. There are special difficulties in connection with short and long lifetimes, materials of low resistivity, etc. The measurements must be taken on slices from a monocrystal, and the preparation of the surface (controlling the surface recombination velocity) can be quite critical.

It is now known that apart from high values of dislocation density, lifetime is controlled largely by group Ib elements present
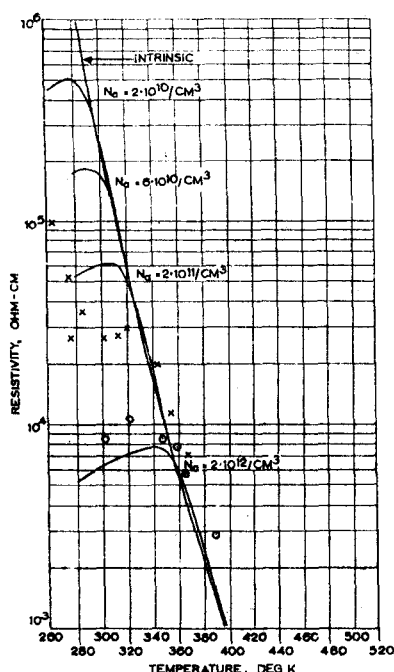
Fig. 2.—Temperature/resistivity characteristics of polycrystalline silicon.

Fig. 3.—Crystal pulling from crucible.

Fig. 4.—Zone crystal growing.

as impurities. Unfortunately these impurities are easily picked up in processes which may occur after the silicon is purified but before it is converted into monocrystal. For example, gold contamination can easily arise from the use of etchants. Badly designed floating-zone equipment can also pump copper into silicon and so reduce the lifetime value.

Modern high-grade germanium and silicon are produced in polycrystalline form and ideally should not require any further purification. However, it is almost impossible, as we have seen, to measure their parameters until they have been converted into monocrystals. There is fairly conclusive evidence that the monocrystal parameters do not reflect accurately the purity of the polycrystalline material prior to crystal growth.

Assuming for the moment that it is possible by modern methods to purify to near the intrinsic state, the outstanding problem would appear to be the conversion of the polycrystalline material to monocrystal with complete control of any further impurities and of the crystal imperfections introduced.

Is this a reasonable target? There are already a multiplicity of crystal-growing methods in production and under study in laboratories and there is already considerable information regarding their performance.

In the case of germanium, since the melting-point is lower than that of silicon and the reaction with crucible and boat materials is very much less, it is customary to use the crucible pulling method (Fig. 3) or the zone method (Fig. 4). With the exception of recent suggestions[3, 4] about oxygen, not much comment has been made in the case of germanium regarding the pick-up of undesirable impurities.

When comparison is made between the two methods the arguments usually revolve round uniformity of resistivity (in which the crucible is alleged to be inferior) and reduction of etch-pit counts. Either method appears to be capable of producing low etch-pit counts (approaching zero).
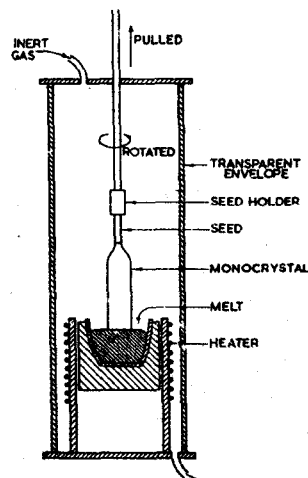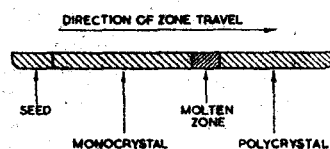
In the case of silicon the situation is quite different. Molten silicon vigorously attacks crucibles and oxygen, and possibly other impurities are incorporated in the crystal. For this reason there has been a decided move away from this technique in recent times. The zone method cannot be used horizontally in boats for the same reason. Since 1953[5] there has been a decided move in the direction of the so-called floating-zone technique with several variants. Here the rod of silicon is maintained vertical and the process of Fig. 4 applied. By suitable arrangement of the r.f. field the molten zone can be maintained without 'breaking' of the rod—at least up to certain diameters ($\frac{3}{4}$ in or so).

One variation is shown in Fig. 5. Here the tip of the rod is melted and the crystal is pulled by adjusting the relative velocities of the top and bottom of the arrangement.

It has been found possible to zone-refine silicon horizontally (but not to produce good crystals) by a device known as the silver boat,[7] in which cooling of the boat and a special arrangement of the r.f. field causes the molten zone to 'lift' from the silver surface.

This is mentioned because there is a growing tendency to use the floating-zone crystal grower as a zone refiner during the crystal-growing process. This meets, partially at least, the requirement postulated earlier for 'cleaning up' the polycrystalline rod before (or during) conversion into monocrystal. It is perhaps a somewhat uneconomic use of a crystal grower.

Criticism about the floating-zone technique has centred to a large extent on the following points:

(a) Limitation of diameter.
(b) Atmosphere—very pure argon or vacuum.
(c) Small volume of molten-zone leading to imperfect crystals.
(d) Effects of r.f. field in possibly causing turbulence in the molten zone.
(e) Care necessary to avoid introducing impurities, e.g. from the r.f. coils.

(b) is of course associated largely with the reduction of oxygen

Fig. 5.—Molten zone and related details in equipment for pulling crystals without crucible.

It is clear, therefore, that in assessing the performance of a given crystal-growing equipment we must carefully examine every detail of the equipment and check carefully, sometimes by a variety of test methods, the characteristics of the crystals produced.

There is some evidence that identical polycrystalline bars used in a variety of crystal growers can produce a variety of crystals. Unless great care is exercised in operation this can also occur for any given grower. This is not to the liking of silicon suppliers who supply polycrystalline bars to users. Most of them have perforce acquired crystal growers of their own. However, if their choice is not of the best and if their operation is not perfect they may come to wrong conclusions regarding the quality of their polycrystalline material.

A fair presumption can be made that at some point in some of the purification processes the purity of the silicon is well above the 1 000 ohm-cm value which at the moment is the required specification. Some suppliers of silicon and some of the large laboratories in this field have evolved chemical and chemical-physical process which must, if carefully handled, raise the value to 10 000–20 000 ohm-cm or higher.

In the last few years the main suppliers of silicon and several important laboratories have throughly studied the problem of purification of silicon. There is general agreement that silicon tetrachloride should be the starting material, and much work has been done on means of purifying this material. There is at at least a majority agreement that the main and final purification should be in the gas phase. Some prefer silane, some trichlorsilane. Much work again has been done on purification of such gases. In my opinion silane offers the greater potentialities.

Next comes the cracking process from which elemental silicon is obtained. Here we reach the point where purity begins to diminish. However, we have by no means exhausted our ingenuity and we may expect that further improvements in this process will result. From this point onwards the improvements are conjectural but they are by no means improbable. So intuitively I see higher and higher values of uncompensated resistivity and of lifetime accruing.

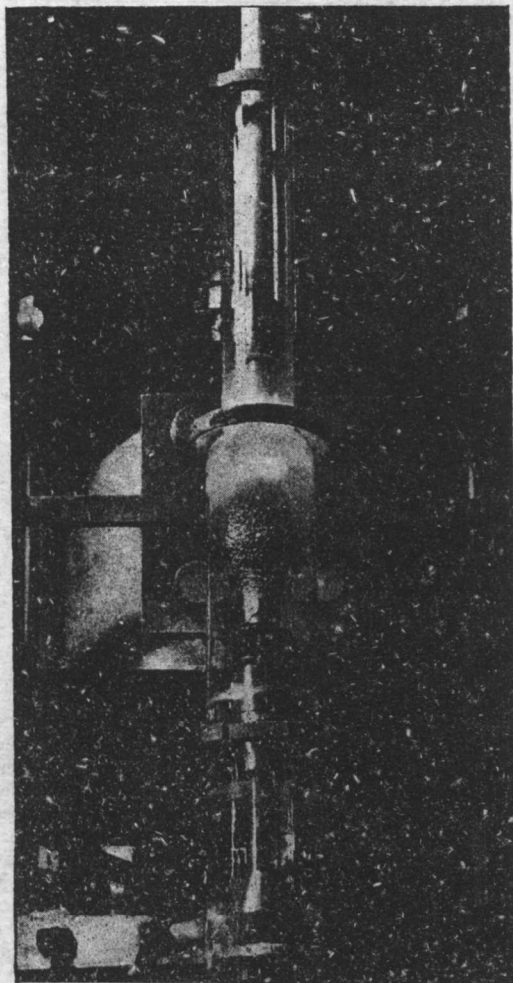It is thought by some that this is useless since doping will reintroduce unwanted impurities, but that problem has already been foreseen and will in due course be dealt with satisfactorily.

It seems clear that we are learning rapidly how to control both germanium and silicon and thereby to diminish, at least, the problems of manufacturing transistors and diodes.

content. (c) and (d) are associated with dislocations and etch-pit counts.

Although it has been possible to produce silicon crystals with no dislocations[6] by using a very small seed (1 mm or less) containing very few dislocations, this in fact refers only to those dislocations which show up as large etch pits. There may still exist small dislocation loops and other imperfections such as chemical precipitates, lattice vacancies and vacancy clusters.

It can be established there there is a one-to-one correspondence between etch pits and at least edge-type dislocations. Dash[6] has shown that copper diffused into silicon precipitates out along the dislocations, which can be observed optically using an infra-red image tube. There are complications in that etch-pit counts depend upon the impurities associated with the dislocations. Further, the presence of oxygen tends to inhibit the development of etch pits. Crucible-pulled silicon crystals usually show a much higher density of etch pits round the circumference compared with the centre. This may be attributed to the evaporation of the oxygen from the outer layer.

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AUXILIARY MATERIALS IN TRANSISTOR TECHNOLOGY

By W. C. DUNLAP.

There are many problems in transistors, and those which seem to be the most critical lie in the control of some of the auxiliary materials which enter into the manufacture of the transistor.

There are two classes of auxiliary materials. The first, and that which is stressed here, is the group of materials which are designed to affect the properties of the primary semiconductor, such as the doping agents in control of conductivity and formation of junctions. The second includes those materials that are required in the manufacturing processing for one reason or another, but which are not intended to have, and which it is hoped will not have, any direct influence on the primary semiconductor.

Among the processes used in the manufacture of the transistor are crystal growth and purification, doping agents, sample and wafer preparation, alloying diffusion, ohmic contacts, etching and rinsing, mounting of base-plates, surface treatment and storage, packaging and encapsulation. Each of these topics involves auxiliary materials within the scope of the present discussion.

The properties of the auxiliary materials are:

Purity.
Physical form.
Physical: thermal expansion, strength and melting-point.
Metallurgical: phase properties and diffusion.
Chemical: corrosion and the effect of etching.
Electrical.
Optical.
Interaction with other materials.

Purity is important, particularly for such materials as alloying agents and doping agents. Physical form is a problem in many cases, although few general statements can be made on this topic. Metallurgical and mechanical properties, such as thermal expansion, strength, melting-point and diffusion coefficient, are of great importance for many of the leading auxiliary materials and for transistor fabrication. Sometimes chemical properties must be considered in deciding whether certain materials can be used.

A most important problem is the interaction of one material with others used in manufacture; in other words, we must examine the compatibility of the material, such as an alloying or soldering agent, with the other materials to be used, in the light of the processing contemplated. A simple example is the case of the ability of an alloying or soldering agent, or the proposed header material, to stand the chemical etching proposed to clean the junctions on the primary semiconductor.

The first auxiliary materials to be considered are the doping agents. These are the materials by which control of type and conductivity of the primary semiconductor is achieved. The doping agents for germanium and silicon fall into the following classes:

(*a*) Group III acceptors, including boron, aluminium, gallium, indium and thallium.

(*b*) Group V donors, including phosphorus, arsenic, antimony and bismuth.

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(*c*) Group I donors, of which lithium is at present the only known example.

(*d*) Group II and Group III acceptors, including silver, copper, gold, platinum, cobalt, nickel, iron, and probably many others.

There are now known to be a large number of impurity elements which affect the electrical properties of, say, germanium. The simplest to understand and use are the III–V elements. These produced *n*- and *p*-type conductivity without affecting lifetime specifically. On the other hand, many of the other elements, because of the deep states they produce scattered through the forbidden energy band, have considerable effect not only on conductivity, but even more so on lifetime and recombination processes. Many of these impurities are important because they also diffuse rapidly and because they can easily be present as contaminants, whether in rinse water, in mounting plates or in furnace gases.
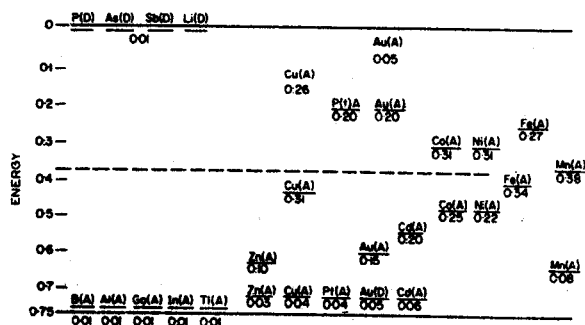
Fig. 1.—Energy levels for various impurities in germanium.
Levels in upper half measured from conduction band.
Levels in lower half measured from valency band.

Fig. 1 indicates the energy levels of some of the known active impurities in germanium. The conclusion can safely be drawn that the main features of the behaviour of the elements in silicon and germanium are now known, although some new properties are probably yet to be discovered. Greater sensitivity in methods of detecting electrical effects of some of the elements in germanium or silicon may be required because of their low solubility.

Among the requirements for a good doping agent are high solubility, so that a wide range of resistivity can be produced, and an intermediate value of segregation coefficient, i.e. the relative amount of the element entering the solid during crystal growth compared with that remaining in the melt. This intermediate value is useful in that it permits reasonable values of doping agent to be used, so that weighing by micromethods is not required, and again in that purity of the doping agent itself is not so critical.

Table 1 shows some segregation coefficients for germanium. These have now been studied extensively, but there still remain

Table 1

SEGREGATION COEFFICIENTS OF VARIOUS IMPURITIES IN GERMANIUM

	Germanium	Silicon
Boron	17	0·9
Aluminium	0·10	
Gallium	0·10	0·01
Indium	0·001	0·0005
Thallium	0·0004	
Phosphorus	0·12	0·35
Arsenic	0·04	0·3
Antimony	0·003	0·04
Bismuth	0·0004	
Tin	0·02	0·02
Copper	0·000015	0·0004
Silver	0·0001	
Gold	0·00003	0·00003
Nickel	2×10^{-6}	
Iron	10^{-6}	
Cobalt	10^{-6}	

gaps in the Table and opportunity remains for good research in the field.

Other characteristics sometimes needed in doping agents are low vapour pressure, freedom from toxicity and low chemical reactivity, so that wetting and solubility are not limited by oxide layers. These desired properties are sometimes difficult to achieve with pure elements, and consequently master alloys of the doping element are sometimes made up so that the amount going into the crystal-growth operation is minimized. Purity can be important if the segregation coefficient is very small.

Of considerable importance as auxiliary materials are the alloying agents. These agents are also required to modify the conductivity, so that the group III–V elements again come into the discussion. Because of the different mechanical, physical and electrical processing required, however, forms and compositions different from those for doping are required for alloying.

Among the important problems in the use of alloying agents are the wetting of the surface, mechanical strength of the junction, correct thermal expansion, proper penetration into the junction region, ability to withstand the etches used to clean the surface of the semiconductor itself and suitability for the addition of soldered or other contacts. For the satisfaction of these sometimes mutually contradictory requirements, many practical investigations on complex alloying agents are being made. This is an area of the semiconductor art as distinct from science in which practical advances are expected to be quite rapid during the next few years. In addition, for diffused systems a scientific basis for these studies is being established by the investigation of phase diagrams for binary, ternary and even more complicated systems of the alloying and other elements of importance.

Table 2 shows some of the alloying combinations used for germanium. Indium, the element used in the very beginning

Table 2

ALLOYING AGENTS FOR GERMANIUM

	Type	Alloying temperature deg C	Carrier
Indium	p	550	
Gallium	p	550	In
Aluminium	p	550	In
Arsenic	n	750	Pb
Antimony	n	750	Pb
Gold-gallium	p	450	Au
Gold-antimony	n	450	Au

of alloyed junctions, remains one of the most widely used in spite of its relatively low solubility in germanium. For the doping of emitter contacts, small additions of aluminium and gallium are now commonly made. Indium doped with arsenic or antimony can be used to produce n-type contacts on germanium, although nowadays it is more common to use lead as the carrier of the active impurity, which is usually arsenic for n-type and indium for p-type contacts. Gold-gallium and gold-antimony are also widely used, particularly in the form of wire for small bonded contacts.

As a typical problem in the use of alloying agents, we mention only that problem associated with the emitter efficiency indicated in Fig. 2. The curve showing current gain as a function of
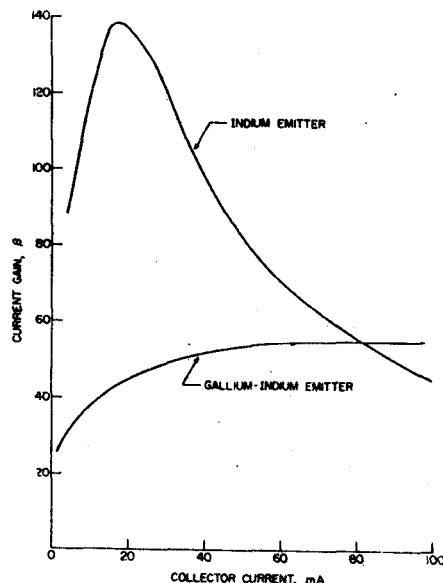

Fig. 2.—Current gain versus collector current for two types of emitter.

emitter current when indium is used possesses a pronounced maximum at small emitter current and a rather pronounced decrease for large emitter current. When gallium-indium emitters are used, the peak is removed and there is a much smaller variation of current gain with emitter current than in the previous case.

We now proceed to the study of diffusion. Diffusion has turned out to be an extremely important and useful technique. The materials used, of course, require the same elements with which we have been dealing in connection with doping and alloying. Again practical requirements dictate the use of forms of elements for diffusion different from those used for doping or alloying. Other more specialized problems occur where diffusion and alloying are used simultaneously in the fabrication of the devices. Because of the high temperatures required for most diffusion operations (typically 850° C for germanium and 1 250° C for silicon) and because of the difficulty of producing reproducible junctions with volatile elements such as phosphorus and arsenic, it has become common to use compounds for the source of diffusion impurities. For boron diffusions, a typical compound is boron-glass containing 30% boric oxide, 10% aluminium oxide, 10% barium oxide and 50% silica. This glassy material is spread over the surface of the silicon or germanium and produces a better junction under many condi-