

July 16, 1963

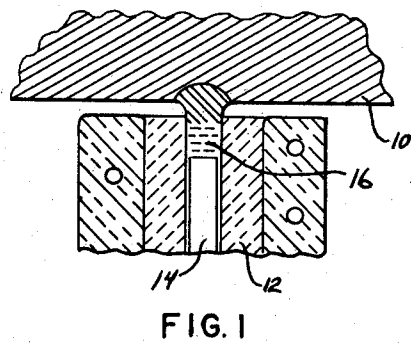
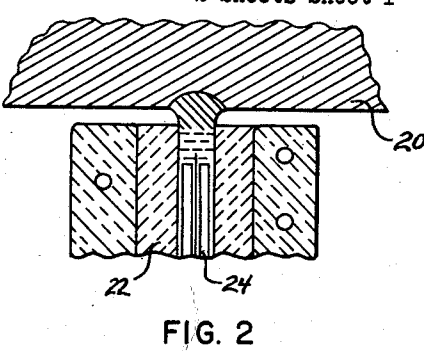
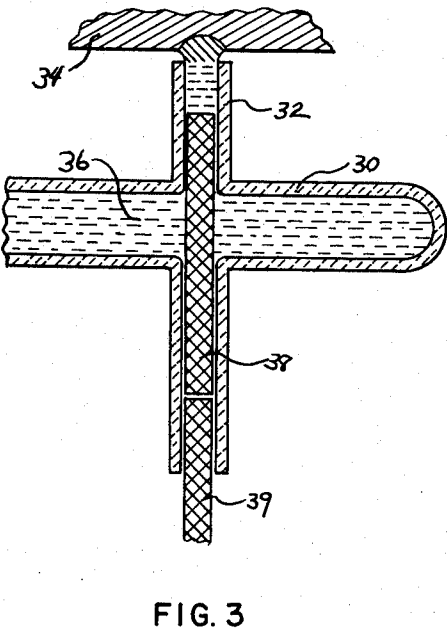
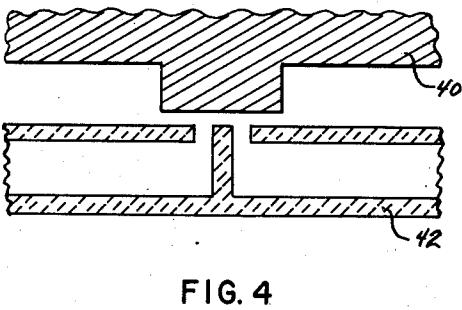
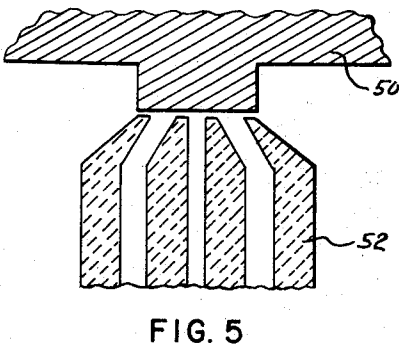
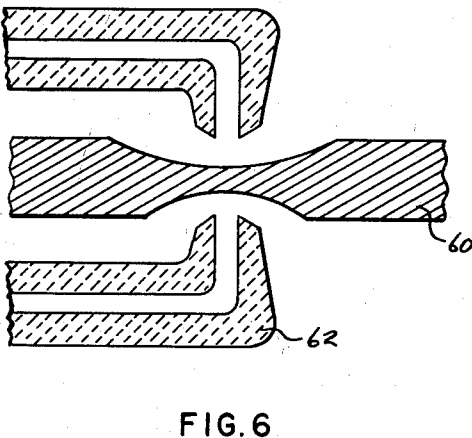
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3,097,976

SEMICONDUCTOR ALLOYING PROCESS

Filed July 6, 1959

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

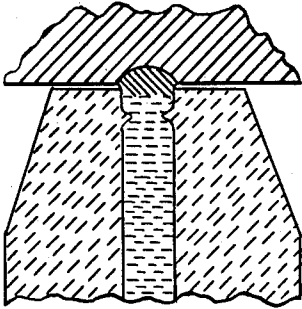


FIG. 7

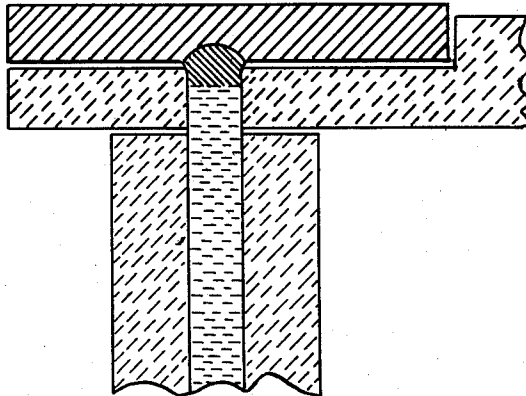


FIG. 10

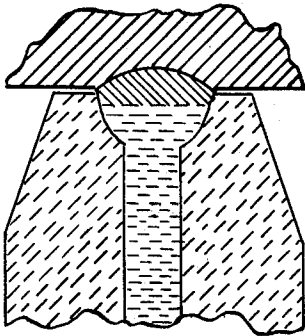


FIG. 8

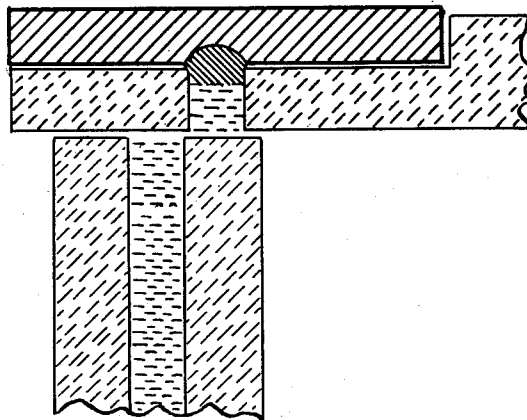


FIG. 11

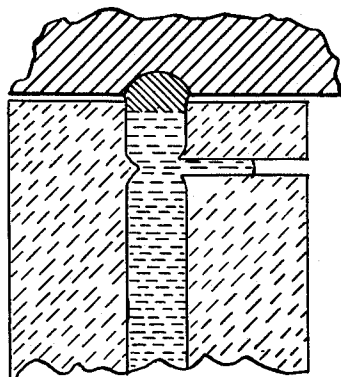


FIG. 9

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3,097,976

SEMICONDUCTOR ALLOYING PROCESS

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2 Claims. (Cl. 148-1.5)

This invention relates to a process for alloying metal to semiconductors, and more particularly relates to producing alloy electrodes by liquid column alloying techniques whereby a small area alloy contact to a semi-conductive crystal is obtained by bringing a droplet of molten metal or metal alloy from a large reservoir into contact with the semiconductive crystal. This application is a continuation-in-part of my Liquid Column Alloying application S.N. 636,821, filed January 28, 1957, and later issued on July 7, 1959, as U.S. 2,893,901.

There are two presently popular semiconductive devices in which the electrical properties are controlled by maintaining control over the lateral extent and the separation of closely spaced electrodes. Control over separation must include control over the depth of penetration of the electrode into the semiconductive crystal. One of these devices is known as the electrochemical transistor, and includes such sub-types as the surface barrier transistor, the microalloy transistor, and the microalloy diffused transistor, and is characterized by a semiconductive crystal having a narrow web produced by jet etching and having emitter and collector electrodes on opposite sides of the narrow web. The fabrication of the narrow web transistor is disclosed in detail in an article by Tiley and Williams in Proc. IRE 41 (12), 1706-1708 (1953).

The other of the two semiconductor constructions that requires careful control over the extent and penetration of electrodes is called the mesa semiconductive device, and is characterized by a flat-top elevated portion (mesa) having steeply sloping walls rising above a surrounding substantially flat surface. Two closely spaced electrodes are plated onto the small area flat-topped portion of the mesa. A suitable method for preparing a mesa transistor having two electrodes on its elevated mesa is described in "New Transistor Design—The Mesa," by C. H. Knowles, in Electronic Industries, pp. 66-60, August 1958.

Recently, a combination of the two above-mentioned types of semiconducting devices has been devised. This new device includes a small area mesa surrounded by a moat or trough that extends into the crystal body toward the opposed face that has been concavely etched by means that is typical of the electro-chemical transistor. The trough extends toward the etched undersurface of the crystal so that the space charge layer at the collector will reach the trough before reaching the emitter contact, thereby "pinching-off" the mesa electrically from the base. This narrow webbed mesa semiconductive device is described in detail in my copending application S.N. 784,632, filed January 2, 1959.

The problems involved in controlling the depth of penetration and the lateral extent of an alloyed contact are very exacting, inasmuch as the penetration can be no more than a few tenths of a mil and the lateral extent of an electrode can be no more than a few mils. One prior art attempt at meeting the problem includes the use of a mechanical jig that is positioned over a face of a semiconductive crystal so as to provide a form or guide that has a controlled area. A solid preform of the material to be alloyed to the crystal is then placed within this guide and a pressure-urged plunger means is inserted within the guide to exert pressure upon the preform while the entire combination is brought to alloying temperature. In another prior art process, a droplet of

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alloy material is permitted to free-fall onto a semiconductor surface. The semiconductor surface and the drop must then be subjected to conventional alloying techniques in order to control the lateral extension of the drop. Neither of these two prior art processes provided a satisfactory solution to the problem, in that the first required time consuming and painstaking handling of tiny preforms, and the second failed to provide satisfactory control over the lateral extent to the drop.

My parent application S.N. 636,821, filed January 28, 1957, discloses and claims a process for producing an alloy junction in a semiconductor body by forcing a drop of molten metal or metal alloy from a reservoir through a restricted column into contact with a portion of a semiconductor body so as to dissolve the contacted portion of the body, and then recrystallizing the resulting liquid phase of droplet and semiconductor.

It is an object of this invention to overcome the deficiencies and shortcomings of the prior art.

It is a further object of this invention to improve upon the process of my prior application.

It is a further object of this invention to provide a process that combines attaching a lead-wire to the liquid column alloying process and construction.

These and other objects of the invention will become apparent from the following description when read in conjunction with the accompanying drawings in which:

FIGURE 1 is a sectional view that is illustrative of the general apparatus and structure of this invention;

FIGURE 2 is a sectional view of a modification of the subject matter of FIGURE 1 having means for attaching a lead-wire to the alloy contact;

FIGURE 3 is a sectional view of another embodiment of this invention wherein a lead-wire is attached to a semiconductor body at the time of providing an alloy contact;

FIGURE 4 is a sectional view that is illustrative of the embodiment of this invention wherein dot or line contacts are applied to a mesa type semiconductor body;

FIGURE 5 is a sectional view illustrative of the embodiment wherein a dot contact and a concentric annular contact are applied to a mesa type body; and

FIGURE 6 is a sectional view illustrative of the embodiment wherein two contacts are applied to opposite surfaces of an etched semiconductor body.

In general the objects of this invention are obtained by a process that comprises bringing a semiconductive wafer into contact with a molten metal alloy column at the mouth of a capillary and then removing the semiconductor and an attached droplet of metal alloy from the vicinity of the capillary to permit recrystallization and solidification of the liquid phase comprised by the molten alloy droplet and the contacted portion of the semiconductor body without requiring contact with the rest of the column of liquid metal alloy.

One of the specific embodiments of this invention involves a process wherein a semiconductive wafer is lowered onto the orifice of a capillary tube, and then a liquid column of molten metal or metal alloy is raised into contact with the wafer, and the contact between the liquid column and the wafer is maintained for a predetermined time and at a predetermined temperature, so that when the wafer is removed from the orifice of the capillary a drop of the liquid alloy remains attached to the wafer.

Another embodiment of this invention involves a process wherein a germanium wafer is positioned at a distance from a capillary that is not greater than the diameter of the orifice of the capillary. In this process a column of liquid alloy is pushed out of the orifice until it comes into contact with the germanium surface, and is retained in contact with the germanium surface for a

short alloying period, after which the germanium is removed from contact with the liquid alloy column with a droplet of the liquid alloy remaining attached to the germanium.

Another embodiment of this invention involves a process wherein a liquid alloy is pushed out of a capillary until a droplet of liquid alloy forms exteriorly of the orifice of the capillary. After this droplet has reached a desired size, the liquid column is withdrawn into the capillary, thereby leaving the droplet positioned on the capillary at the orifice. A germanium wafer is then brought into contact with this free-standing droplet so as to adhere the droplet to the germanium wafer. A conventional heat treatment may then be employed to obtain the proper depth of alloying. One of the advantages of this embodiment of the invention, wherein a free-standing droplet of liquid alloy is first produced and then is attached to the germanium wafer, lies in the fact that removal of the droplet from the capillary by adhesion to the germanium does not have to contend with the problem of breaking the surface tension that exists between the droplet at the mouth of the capillary and the rest of the liquid column. By this simple expedient, it has been found that even a small amount of initial wetting is sufficient to adhere the droplet to the germanium surface.

Another embodiment of this invention involves another process and apparatus wherein two liquid alloy contacts are produced in close proximity to one another on the surface of a semiconductor. By utilizing simple modification of the apparatus, these contacts may be positioned on opposite sides of a thin wafer by positioning the two capillaries in a coaxial arrangement with orifices facing each other. In the case of mesa type transistors, two alloy contacts in close proximity are required on the same surface of the semiconductor. This embodiment permits the application of one dot electrode with one ring electrode concentric thereto. Another feature of this embodiment is that two closely spaced line contacts can be provided in a highly reproducible manner.

FIGURE 1 shows an apparatus that may be used in single or multiple units to provide alloy contacts to semiconductor bodies. A capillary tube 12 is positioned against, or within the capillary diameter, of semiconductor body 10. Capillary 12 is filled with liquid metal or metal alloy material 16 and is provided with a plunger or piston 14 for forcing a single droplet of material 16 from the orifice of capillary 12 into pressure contact with semiconductor body 10. This liquid alloying equipment preferably uses a capillary with perforated walls through which the liquid metal or metal alloy may enter from a large reservoir. The piston 14 may be controlled by micromanipulation to force the molten liquid material through the orifice of the capillary so as to permit the formation of a single droplet.

Among the various techniques that are employed with this structure is the process wherein semiconductor body 10 is lowered onto the orifice of the capillary and then the liquid column within the capillary is raised by means of plunger 14 so as to establish a pressure contact to the body 10. This pressure contact is maintained for such time and temperature as to effect dissolution of a small quantity of body 10 in the alloying material. The pressure is then withdrawn to permit the liquid column to recede and thereby break off the droplet that is in contact with body 10. After recrystallization has been effected, the semiconductor body and alloyed contact are removed.

Another technique involves locating the body 10 at a distance from the orifice that is no greater than the diameter of the orifice. The liquid alloy is then pushed out of the orifice until it touches the surface of body 10. After a short alloying period the semiconductor body is removed from contact with the liquid column, thereby effecting the removal of a droplet of the alloy from the

column. The size of this droplet depends upon the spacing between the body and the orifice of the capillary. Another technique involves pushing a droplet of the alloy out of the orifice until the droplet rests on the top of the capillary and then withdrawing the liquid column leaving the droplet free. The semiconductor body is then brought into contact with the droplet and is maintained against the droplet until a sufficient wetting is obtained so that removal of the semiconductor body will remove the droplet from the capillary surface.

It has been found that capillary tube 12 may be made of carbon, glass or quartz. The internal diameter of the capillary is preferably about 5 mils or less. The molten metal or metal alloy can be an indium-germanium alloy in ratios of about 2:1 to about 40:1 parts by weight, with the optimum properties obtained with the composition of 20 parts indium to 1 part germanium (germanium is added to prevent the indium from dissolving an unnecessary amount of germanium from the semiconductor body). The amount of germanium which can be added to the alloy is limited as a practical matter because germanium raises the melting point and decreases the ductility of the alloy. In order to keep the liquid alloy material from solidifying in the capillary, it has been found advantageous to surround the capillary by a jacket or insulation which may contain an electric heating coil. This structure is explained in detail in my above-identified parent application.

Thus, it is seen that the capillary 12 of my invention serves a plurality of useful purposes including providing an efficient means to guide the alloy material to the semiconductor, as well as providing a means to limit and control the contact area, and in addition provides an efficient means for applying pressure to maintain the alloy in contact with the semiconductor body during the alloying cycle. For the purposes of this invention, the term alloying cycle refers to the temperature-time relationship of the liquid alloy to semiconductor body contact. This time-temperature relationship determines the depth of alloying in accordance with well-known principles in the semiconductor art.

The apparatus shown in FIGURE 2 is similar to the apparatus shown in FIGURE 1 with the addition of a bore within the plunger or piston 24. This bore permits a wire to be fed through the piston and through the orifice of the capillary into contact with the alloy droplet on the semiconductor body. Upon freezing of the alloy droplet, the wire becomes firmly attached and can be cut to a desired length. This apparatus permits the attainment of an alloy junction and a lead-wire attachment in a one step process. As is the case of all of the examples in this description of my invention, the apparatus of FIGURE 2 may include provisions for providing a plurality of like contacts to a single semiconductor body.

The apparatus shown in FIGURE 3 enables another process to be employed in providing an alloy dot and a lead-wire to a semiconductor body. The apparatus and process that may be described with respect to FIGURE 3 is particularly useful for the fabrication of high power transistor bodies requiring a high degree of heat dissipation, wherein it is advisable to have a lead-wire contact of high heat conductivity, preferably a rod of a diameter close to that of the alloy contact to the semiconductor body. For example, an alloy contact in the form of a circular area of ten mils diameter on a germanium body permits optimum efficiency when provided with a rod of silver approximately 8 mils in diameter. A means by which the silver rod can be connected to the contact in a convenient efficient and precise manner is shown in FIGURE 3, wherein a tube 30 is provided with a capillary 32 having an internal diameter of the desired size of contact to be applied to semiconductor body 34. Tube 30 is filled with alloy material 36 similar to that previously described. This alloy material is kept molten by heating coils and insulation as has also been pre-

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viously described. Tube 30 is provided with a tubular extension opposite a capillary extension 32, so as to provide a slide chamber for a piston member 39. A lead-wire 38 of suitable size is pushed through the opposed bores into contact with the liquid alloy droplet against semiconductor body 34. Thereafter, pressure may be maintained by means of a separate plunger 39 or by means of lead-wire 38. The amount of alloy material 36 between lead-wire 38 and semiconductor body 34 is preferably reduced to a thin film of alloy that is kept on the lead-wire 38 by surface tension (wetting), to provide mechanical strength and heat conduction. The substantial amount of alloy between the lead-wire and the semiconductor body shown in FIGURE 3 is for the purpose of clarity only.

FIGURES 4, 5, and 6 are designed for applying plural contacts to special transistor semiconductor constructions. In the preparation of mesa type transistors two alloy contacts are desired on the small area surface at the top of the mesa. These contacts require a close spacing of alloys of different compositions. The structure shown in FIGURE 4 permits placing two dot or line contacts side by side on a mesa, while the equipment shown in FIGURE 5 permits the placing of a ring type contact around a dot contact. The equipment shown in FIGURE 6 is specifically designed to place dot contacts on directly opposite surfaces of a narrow web transistor described in the above referenced Tiley and Williams publication.

A specific example of the process of this invention includes the preparation of an n-type germanium wafer with surfaces in the crystallographic (111) direction and containing antimony as an impurity to provide a resistivity of one ohm centimeter. The crystal is lapped to a thickness of five mils and then etched in a hydrofluoric-nitric-acetic mixture to a thickness of three mils. The wafer is picked up by a suction tube and placed over the polished plain surface of a glass capillary of 10 mils internal diameter (approx. 100 mils outside diameter) contained in an inert atmosphere such as argon. The glass capillary is connected to a glass reservoir containing molten indium. The liquid indium is forced against the surface of the germanium wafer which has closed the orifice of the capillary by exerting pressure by means of a mechanical plunger or an inert gas pressure. A gas pressure of 40 centimeters of mercury has been found satisfactory for this purpose. The liquid indium is kept at a temperature of 250° C. and the germanium body is kept at a temperature of 200° C. Contact of the liquid indium to the germanium is maintained for thirty seconds and then the indium is withdrawn in the capillary by decreasing the pressure. This leaves a droplet of indium on the germanium surface, which solidifies upon removing the germanium from the orifice of the capillary.

An interesting embodiment of this invention involves drawing an indium wire in contact with an indium alloy contact to a germanium wafer. In order to accomplish the wire drawing, the pick-up suction tube described in the preceding paragraph is provided with tiny holes which permit blowing cool argon gas through the suction tube after the germanium is in contact with the liquid indium. By proper balancing and manipulation of the heating and cooling rates, a column of indium in the capillary adjacent to the germanium can be solidified and the germanium together with this column can be removed from the capillary by utilizing suction in the suction tube as a pulling agent.

Various additional process embodiments are practical with the apparatus shown and described. For example, a p-n-p structure may be obtained by starting with a p-type germanium wafer and alloying thereto a dot of an alloy containing 97% indium and 3% arsenic. Inasmuch as the indium does not diffuse as rapidly in germanium as does arsenic, the n-type zone is formed adjacent the

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p surface of the germanium wafer and is then overlaid with a p surface.

Another process embodiment of this invention involves the use of an alloy containing a doping agent for the crystal, as well as a carrier chosen for its phase diagram and for its physical properties, for example expansion, softness. Typical alloys for p-junctions to n-type germanium include indium, indium-gallium, and indium-aluminum; alloys for n-junctions to p-type germanium include lead-arsenic and lead-antimony. These same alloys are also suitable for use on silicon crystals.

In order to produce well defined recrystallization of the liquid phase consisting of the alloying material and the dissolved portion of the semiconductor body, it has been found to be advantageous to utilize the well-known Peltier effect. A discussion of Peltier heating and cooling resulting from passing a direct current between a liquid and a solid is found in an article entitled "Some Aspects of Peltier Heating at Liquid-Solid Interfaces in Germanium," by W. G. Pfann, K. E. Benson, and J. H. Wernick in *Journal of Electronics (Eng.)* (1st series) 2, 597-608 (1956-1957). In the specific example recited above, wherein the molten material is indium and the semiconductor body is n-type germanium, the piston 14 is made of carbon to permit the connection of the positive side of a D.C. supply to the indium while the germanium is made negative, whereby passage of current will produce a cooling effect at the interface.

In work done toward improving the reproducibility of devices produced according to this invention, it was discovered that breaking the column of liquid alloying material from the resolidified contact on the semiconductor body sometimes resulted in pulling varying amounts of material from the contact to the body. This meant that even though withdrawing the pressure producing means resulted in a break-off of the liquid column at some point within the capillary, the break-off did not always occur at the desired position. The mechanism involved in a faulty break-off of the liquid column is believed to result from the tight seal that exists between the liquid column and the inside walls of the capillary. When the pressure producing means is released or withdrawn, the column will break off at some point, thereby leaving an empty space or vacuum between the column and the material that has adhered or alloyed to the semiconductor body. This vacuum coats with the atmospheric pressure outside the capillary to provide a suction. This sudden suction can pull down some of the adhered alloying material to such an extent that even when successive break-offs occur at one point, different amounts of alloying material may be drawn down, thereby lessening the probability of reproducibility in the process.

Various techniques and equipment have been developed to ensure reproducibility of the break-off point. These developments are illustrated in FIGURES 7 through 11, which show a plurality of means for effecting break-off of the liquid column at the exact point desired for optimum results. The constructions shown in FIGURES 7, 8 and 9 have the common feature that may be defined generally as break-off means having a small radius of curvature whereby a high surface tension may be obtained. These break-off means are so constructed as not to be wet by the liquid alloying material. In FIGURE 7 the means comprises a constriction near the top of the capillary. This constriction may involve the simple reduction of the internal diameter of the capillary at the desired point, or may comprise a plurality of projections that extend into the capillary. In FIGURE 8 the means to break the column is shown as a hemispherical orifice at the top of the capillary. While the FIGURE 8 illustration is of a true hemispherical orifice, it should be understood that other shapes are within the concept of this feature of the invention.

The FIGURE 9 means to break the column of liquid

alloying material at the desired point is shown as a side vent or capillary of smaller diameter than the main capillary. This side vent passes through the wall of the main capillary tube so as to permit the inert atmosphere surrounding the apparatus to enter on the column, thereby avoiding the vacuum situation described above. This side vent also provides the desired geometry of having a small radius of curvature to assist in locating the break-off at a given point in the main capillary. It has been discovered that this side vent also acts as a pressure gage which reveals the amount of pressure being exerted on the liquid column by revealing the amount of alloying material that has been forced into the side vent. In this regard, it should be noted that the surface tension of the liquid column is such that under ordinary pressure almost no material will enter the side vent. This pressure gage aspect of the side vent is important when alloying in a blind cavity such as is produced in the electrochemical transistors shown in FIGURE 6. The side vent also permits the use of a wire or slide-rod to mechanically break into the liquid column.

FIGURES 10 and 11 show two positions of another means to remove a controlled amount of liquid alloying material from a liquid column that is in contact with a semi-conducting body. This structure includes a diaphragm or carrying member which supports and positions a semiconductor body relative to a channel in the diaphragm. When the diaphragm and semiconductor body are positioned as shown in FIGURE 10, with the channel in axial alignment with the liquid column within the capillary tube, it is possible to exert pressure on the liquid column to force the alloying material through the channel into contact with the semiconducting body and thereby effect an alloy junction as described in the preceding examples of this invention. In this regard, the diaphragm serves all of the functions previously served by the capillary tube, e.g., a form to limit the lateral extent of the contact. The surfaces of the diaphragm and the orifice of the capillary may be so constructed and arranged as to provide a slide-fit whereby no alloying material can escape through the joint, and whereby the column of alloying material may be cut by lateral displacement of the diaphragm and the capillary. FIGURE 11 shows the diaphragm and the capillary after relative movement has taken place so as to break the column cleanly at the desired point without pulling any of the material from the channel of the diaphragm, thereby providing a high degree of reproducibility of alloy contacts.

Since the time during which the liquid alloy is kept in contact with the semiconductor body is quite short, it is frequently desirable to assure uniform wetting of the semiconductor body by plating the surface of the semiconductor with a metal film, e.g., indium, which then dissolves during the liquid alloying process.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments herein described except as defined in the appended claims.

What is claimed is:

1. In a process of producing an alloy junction in a semiconductor body, and the attachment of a lead wire in interrelated steps, the steps comprising providing a plurality of closely spaced capillaries, connecting said capillaries to a reservoir of a molten material capable of changing the conductivity of a semiconductor body, positioning a semiconductor body within one capillary diameter of said plurality of capillaries, passing a wire through at least one of said capillaries, exerting pressure on said molten material to force said material through at least one of said capillaries into contact with said semiconductor body and said lead wire and thereby dissolving the contacted portion of said semiconductor body in said material, crystallizing the liquid phase consisting of said material and said dissolved semiconductor body, with said wire in contact with said crystallizing liquid, maintaining said capillaries in position until the alloy contacts are solidified so as to prevent spreading of the contacts, breaking off the column of molten material after wetting of said semiconductor body to leave an empty space between the column and the alloyed materials, and whereby in an integrated process a conductivity junction is produced with a wire secured thereto.

2. The process of claim 1 wherein said crystallizing of the liquid phase is effectuated by passing a direct current between said molten material and said semiconductor body of a polarity to obtain Peltier cooling.

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