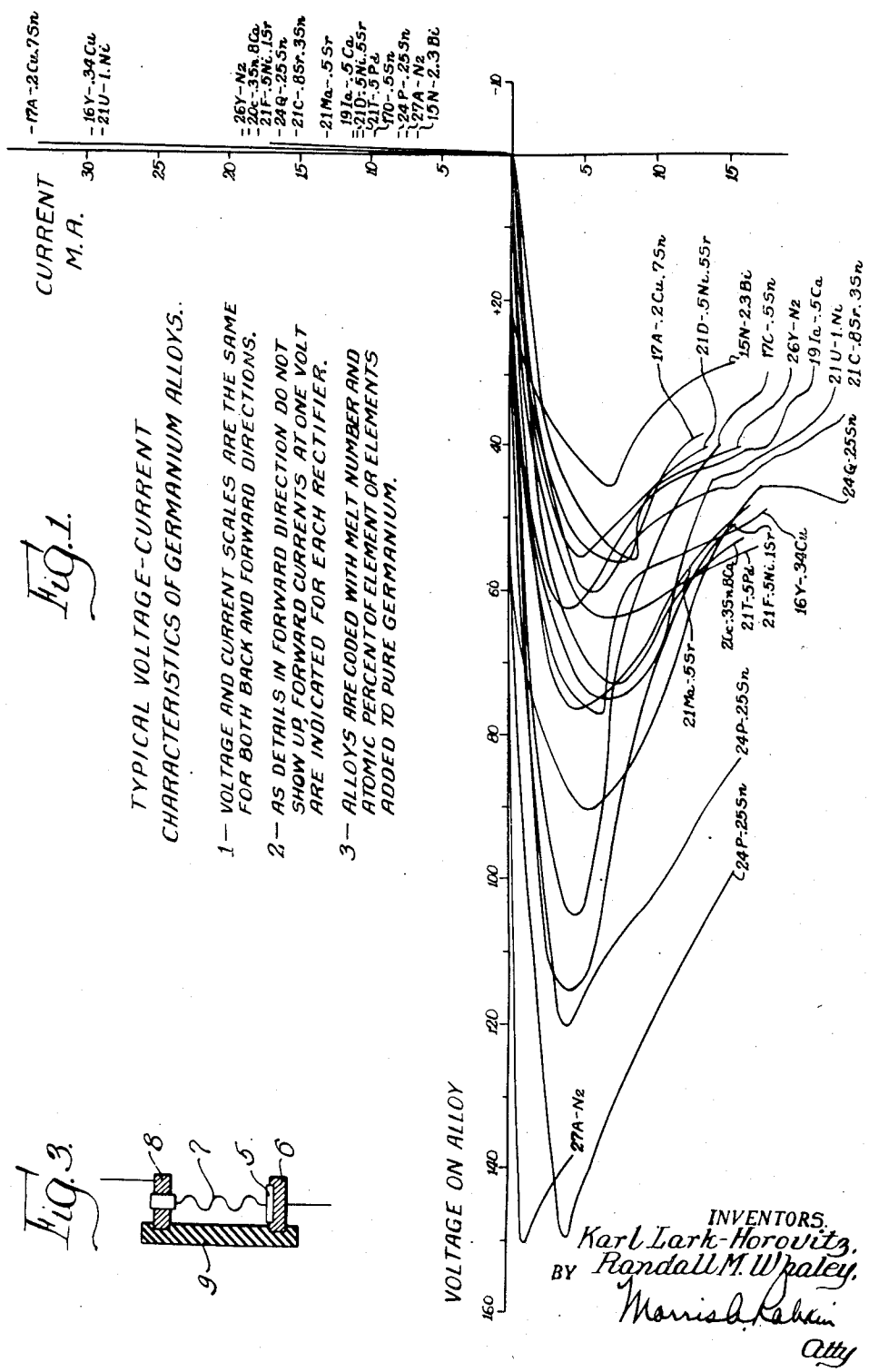
Oct. 28, 1952 K. LARK-HOROVITZ ET AL 2,615,966

ALLOYS AND RECTIFIERS MADE THEREOF

Original Filed July 13, 1945 2 SHEETS—SHEET 1



TYPICAL VOLTAGE-CURRENT CHARACTERISTICS OF GERMANIUM ALLOYS.

1 — VOLTAGE AND CURRENT SCALES ARE THE SAME FOR BOTH BACK AND FORWARD DIRECTIONS.

2 — AS DETAILS IN FORWARD DIRECTION DO NOT SHOW UP, FORWARD CURRENTS AT ONE VOLT ARE INDICATED FOR EACH RECTIFIER.

3 — ALLOYS ARE CODED WITH MELT NUMBER AND ATOMIC PERCENT OF ELEMENT OR ELEMENTS ADDED TO PURE GERMANIUM.

Fig. 1.

Fig. 3.

INVENTORS.
Karl Lark-Horovitz,
BY Randall M. Whaley.
Morris A. Kahn
Atty

Oct. 28, 1952 K. LARK-HOROVITZ ET AL 2,615,966

ALLOYS AND RECTIFIERS MADE THEREOF

Original Filed July 13, 1945 2 SHEETS—SHEET 2

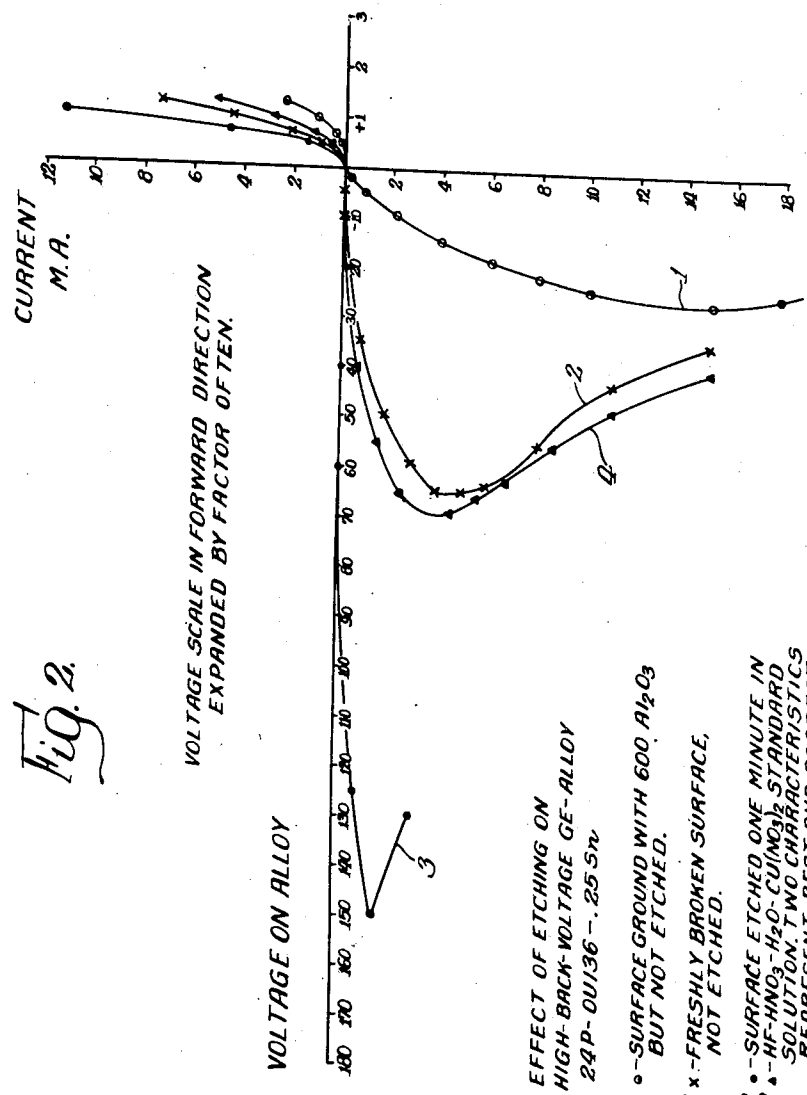


Fig. 2.

INVENTORS
Karl Lark-Horovitz,
BY Randall M. Whaley,
Morris A. Labin
Atty

Patented Oct. 28, 1952

2,615,966

UNITED STATES PATENT OFFICE

2,615,966

ALLOYS AND RECTIFIERS MADE THEREOF

Karl Lark-Horovitz and Randall M. Whaley, La Fayette, Ind., assignors to Purdue Research Foundation, La Fayette, Ind., a corporation of Indiana

Original application July 13, 1945, Serial No. 604,744, now Patent No. 2,514,879, dated July 11, 1950. Divided and this application December 29, 1949, Serial No. 135,746

15 Claims. (Cl. 175—366)

1

This application is a division of application, Serial No. 604,744, filed July 13, 1945, now Patent No. 2,514,879, issued July 11, 1950.

The present invention relates to an improvement in alloys of germanium, and more particularly to rectifiers of electricity, which offer low resistance to current flow in one direction therethrough and high resistance to current flow in the opposite direction, made of such alloys.

In the detailed description of our invention following hereinafter, it will be observed that several of the elements which may be combined with germanium are not metals so that the resultant materials are not alloys in the common meaning of the word. However, for purposes of the present disclosure, it is to be understood that the word "alloy of germanium" as used herein, means to include a union of two or more elements, one of which is germanium, and the other or others being metals, non-metals, or gases, and the combination of which exhibits electrical properties such as are found in metals and semi-conductors.

The known contact rectifiers, i. e., rectifiers comprising suitable metal electrodes, and a semi-conductor have at least one of the following disadvantages:

1. Inability to withstand in continuous use voltages in the back or high resistance direction greater than about 10 volts without permanent injury to the rectifier.

2. Inability to pass sufficient current in the forward direction for satisfactory operation of associated apparatus.

3. Low back resistance prohibiting use of the rectifier in high impedance circuits, that is, circuits over about 100,000 ohms.

4. Seriously decreased efficiency in rectifying at frequencies greater than about 1 to 5 megacycles.

5. Capacity too high to allow efficient operation at frequencies greater than about 5 megacycles.

Due to the aforesaid deficiencies of these known contact rectifiers, the art turned to wide-

2

spread use of vacuum tube diodes for rectifying alternating currents. However, vacuum tube diodes, while overcoming certain of the aforementioned disadvantages of the known contact rectifiers, in turn have the following disadvantages:

1. Inter-electrode capacities which are seriously objectionable at high frequencies.

2. Low forward direction conductance.

3. Requirement of power for heating a cathode.

4. Require a large amount of space as compared to a contact rectifier.

The germanium alloys of our present invention may be used as the semi-conductors for rectifiers of the contact type, which, according to one embodiment of our invention, possess the following general advantages over known contact rectifiers:

1. Ability to withstand continuous operating voltages greater than 10 volts in the back direction, and some of which are capable of withstanding voltages in the back direction of an order approaching 200 volts.

2. Low forward resistances, for example, 30 to 100 ohms at one volt.

3. High back resistances, at about 4 volts ranging from about 10,000 ohms to several megohms.

4. May be used with frequencies up to 60 megacycles and will still rectify at 3,000 megacycles.

5. Provide rectifiers of low capacity of about 0.5 micromicrofarads.

6. Less than 50% decrease in peak back voltage when ambient temperature increases from 23° C. to 75° C.

7. Do not require power for heating a cathode; and

8. Do not require more space than about that needed for a common one-half watt carbon resistor.

The germanium alloys herein disclosed are all of the class of N-type semi-conductors, i. e., semi-conductors which when made into contact type rectifiers present a high resistance to current flow across the rectifying contact when the semi-conductor is positive and the contacting

metal electrode or whisker is negative, and a lower resistance when the potential is reversed.

The various germanium alloys of our invention will be described and compared according to the properties they exhibit when made into contact type rectifiers. Specific electrical properties hereafter referred to are:

Peak back voltage: The voltage-current characteristics measured on rectifiers using the alloys of our invention show a voltage peak in the back or high resistance direction. This peak generally occurs within a range greater than 10 volts and approaching the order of 200 volts. It will also appear that all of these rectifiers using alloys of our invention exhibit a negative resistance region in the back direction for currents exceeding the current at the peak back voltage

Back resistance: In the back or high resistance direction these rectifiers have resistances ranging from the order of 10,000 ohms to several megohms as measured at about 5 volts. High resistances are substantially maintained nearly to the peak back voltage

Forward conductance: The currents passed at one volt in the forward or low resistance direction for these rectifiers generally lie within the range between 5 milliamperes and 40 milliamperes. Actually, somewhat higher currents may be permitted to pass in the forward direction without impairment of the rectifying contact. As will be described later herein, currents greater than 100 milliamperes are sometimes deliberately passed momentarily in the forward direction to produce improvement in certain contact characteristics

The N-type semi-conductors of our invention comprise germanium having small amounts of one of the following elements or certain combinations thereof alloyed therewith:

Copper and silver of column 1 of the periodic table;

Magnesium, calcium, zinc, strontium, cadmium, or barium of column II of the periodic table;

Titanium, tin, or lead of column IV of the periodic table;

Nitrogen, vanadium, columbium, tantalum, or bismuth of column V of the periodic table;

Chromium or uranium of column VI of the periodic table.

Cobalt, nickel, or palladium of column VIII of the periodic table.

N-type semi-conductors of germanium may also be formed by alloying small amounts of, for example, phosphorous, arsenic, or antimony with germanium, but in rectifiers using such semi-conductors it has been found that excessive currents pass at voltages greater than about 3 to 10 volts in the back direction which permanently injure the rectifying contact. It will be understood therefore that our present invention only relates to semi-conductors of the N-type which exhibit high back voltage characteristics in excess of at least 10 volts, and does not concern all N-type semi-conductors consisting of an alloy of germanium, as for example, the group last referred to.

Other features and advantages of our invention will appear from the detail description.

Now, in order to acquaint those skilled in the art with the manner of making alloys in accordance with our invention, and the utilization thereof as rectifiers of electricity, we shall describe in connection with the accompanying drawings and the tables following hereafter certain of the processes used in making the alloys which lie within our invention.

In the drawings:

Figure 1 shows the voltage-current characteristic curves of several rectifiers using certain of the alloys of our invention, which curves are not to be taken as typical of given alloys but merely to represent the type of characteristic exhibited by such alloys in general.

Figure 2 is a graph illustrating the electrical characteristics of rectifiers using different types of surfaces on one alloy of our invention.

Figure 3 is a sectional view of a rectifier, the semi-conductor of which comprises an alloy of our present invention.

Each alloy represented by the curves of Figure 1 is designated by a code number. The latter part of each code denotes the amount in atomic percent of the particular element or elements added to germanium to produce that alloy. No atomic percentage figures for the addition of nitrogen to germanium are given since it is difficult to determine accurately the amount or number of nitrogen atoms alloyed with the germanium.

In the following Table I there are set forth minimum, average, and maximum values of peak back voltage and forward current obtained on rectifying contacts using certain germanium alloys which we have made in accordance with the general procedure to be described later. The amount of the added element alloyed with germanium is set forth for each melt in atomic percent, i. e., the proportionate number of atoms in percent of the elements added to the total number of the atoms of germanium and added elements present. For purposes of adequately setting forth and claiming our invention, these additions to germanium are to be understood as being included in the term "group A" used hereinafter. Substantially all melts in which the addition consisted of a single element made to date in accordance with our invention are contained in Table I. It will be observed from that table that a large number of melts with certain added elements were prepared and it will be understood that the results given are the average results of all of the melts in each instance. It is to be understood, however, that the spread or range of values given in connection with each of the elements added to germanium might not be true for any particular melt of such addition agent. Characteristics for rectifying contacts on any given alloy will lie somewhere within the range given. Further, all points on any given alloy listed in Table I and Table II, referred to hereinafter, will not exhibit the same electrical characteristics. Points may be found on each of the alloys disclosed at which the peak back voltages, back resistances, or forward currents lie in the lower regions of the ranges given above for these values. Also on the same surface of each alloy other points of contact may usually be found with electrical characteristics which lie toward the upper limit of the ranges above set out. However, as will later be discussed in more detail, some of the alloys are of greater uniformity than others with respect to rectification characteristics.

TABLE I

Additions to germanium

[In atomic percent.]

Additions and percentages	Peak Back Voltage (volts)			Forward Current at one volt D. C. (milliamperes)		
	Min.	Ave.	Max.	Min.	Ave.	Max.
Ba: .40, .50	15	50	125	7	13	19
Bi: 1.0, .20, 1.25, .70, .28, .20, .31, 2.0, 2.3, 2.3, .023, .20, .80, .10, .40, .20, .80, .80	15	50	125	7	13	19
Cd: .90, .30	20	50	105	8	12	16
Ca: 2.0, 1.35, .80, .50, .50, .28, .28, .80, .80, .80, .80, .80, .80, .80, .80, .80	25	75	150	5	15	25
Cr: .045, .50	5	15	25	5	15	25
Co: .50	20	30	35	10	15	20
Cb: .20, .43, .045	15	25	40	5	15	40
Cu: .60, 2.00, .42, .19, .34, .37, .40	15	40	75	1	5	40
Pb: 3.0, .80, .50, .13, 1.08, .35	25	70	135	1	15	25
Mg: 3.0, 3.0	10	60	115	2	10	20
Ni: 1.25, .10, .50, 1.0, 1.0, 1.0, 1.0, 1.0	20	50	90	7	15	30
N_2: Solidified in N_2 at pressures of 2, 18, 600, and 760 mm. Hg	20	80	160	7	10	25
Pd: .50, .50	30	65	110	5	15	25
Ag: .66, .50	25	40	80	7	10	20
Sr: .50, .50, .80, .80, .80, .50, .50, .50, 1.0, 1.0, 1.0, 1.0, .50, .50, .50, .50, .50	25	75	150	5	10	25
Ta: .44	20	40	70	3	15	30
Sn: .50, .45, .82, .50, .50, .25, .05, .06, .10, .10, .75, .75, 1.15, 2.80, .75, .78, .90, .90, .75, 2.20, .82, .80, .80, .40, .80, 1.60, .80, .88, .80, .80, .80, .80, .75, .80, .80, .50, .80, .80, .80, .83, .10, 8.0, 17.0, 9.3, .80, 1.20, 1.0, 1.0, 1.0, 1.0, .10, .05, .10, .10, .10, .15, .15, .50, .25, .25, .25, .40, .40, .40, .40, .40, .40, .40, .40, .40, .40, .40, .40, .40	25	75	150	2	15	30
Ti: .50, .50	10	30	70	3	7	15
U: .09, .09	20	25	50	2	5	20
V: 1.0, .15	10	25	65	10	25	40
Zn: .60, .30	25	50	100	5	12	20

In Table II below there are set forth the melts in which two elements have been alloyed with germanium. The additions of these combinations of elements are also set forth in atomic percent as previously defined. It will be understood that the alloys set forth in this table are also to be included in the term "group A" above referred to for purposes of claiming our present invention. The peak back voltages and the forward currents at one volt of rectifiers made of these alloys are also set forth in this table.

TABLE II

Melts of more than one addition to germanium

[In atomic per cent.]

Additions and percentages	Peak Back Voltage (volts)			Forward Current at one volt (milliamperes)		
	Min.	Ave.	Max.	Min.	Ave.	Max.
.20 Bi, .20 Sn	20	25	50	8	15	25
.35 Cu, .70 Sn	25	40	150	15	20	30
.21 Cu, .66 Sn	15	50	80	15	22	50
.21 Cu, .98 Sn	15	40	65	15	30	60
.80 Ca, .30 Sn	50	70	110	5	14	20
.80 Sr, .30 Sn	50	70	100	6	15	35
.50 Ni, .50 Sr	55	75	100	9	30	30
.50 Pd, .80 Sr	35	65	90	8	15	25
.50 Pd, .80 Sr	35	50	95	5	12	20
.50 Ni, .10 Sr	39	50	95	8	15	25
.50 Ni, .30 Mg	20	50	75	12	20	40
.50 Ni, .30 Cu	25	45	75	10	20	35
.50 Ni, .50 Sr	30	40	50	9	12	14
.50 Ni, .50 Sr	15	25	35	10	15	20
.50 Ni, 1.00 Sr	60	90	160	10	15	25
1.00 Ca, 1.00 Sr	10	30	50	13	20	25
.30 Mg, .50 Sr	10	30	45	10	20	40
1.00 Ni, .50 Sr	30	65	100	7	10	18
1.20 Sn, .32 Sr	20	100	165	6	13	19
1.20 Sn, .32 Sr	15	90	100	6	10	15
1.00 Ni, .50 Sn	30	70	110	15	20	25
1.00 Ni, .50 Sn	15	50	90	1	9	19
.80 Ca, .40 Cu	35	75	140	2	7	9
.80 Ca, .40 Cu	15	40	75	3	5	7
.10 Sn, .40 Ca	70	100	175	8	15	24

The germanium alloys of our invention may be prepared in all cases except for the germanium-nitrogen alloy, by melting pure germanium with the desired alloying element or combination of elements in either a high vacuum of the order of 10^{-5} mm. mercury at about 1000° C. or in an atmosphere of helium. Precaution should be taken to prevent the accidental introduction of unknown and perhaps detrimental impurities into the melt from sources such as the crucible or boat in which the ingredients are disposed for melting, the furnace itself, or some material volatilized in the furnace. Alloying germanium with nitrogen may be effected by melting the germanium in an atmosphere of nitrogen which may be either purified nitrogen or nitrogen direct from a commercial cylinder. The germanium is melted in nitrogen at pressures ranging from about 2 mm. to 760 mm. Hg at a temperature of 1000° to 1050° C. Good results appear to be independent of pressure and melts prepared within the above range of pressures were all satisfactory.

The germanium successfully used for these alloys had purity approaching 100%, and electrical resistivity greater than about one ohm cm. The germanium which we have successfully alloyed with other elements to form the alloys listed in Tables I and II was prepared from GeO_2 obtained from the Eagle-Picher Lead Company of Joplin, Missouri. The oxide was reduced in an atmosphere of commercial hydrogen at temperatures of 650° to 700° C. over a period of three to four hours. The oxide reduced in this manner leaves the germanium metal in the form of a gray-green powder which is then alloyed with another element or elements in the manner and proportions described.

The aforesaid melts of germanium and the added element or elements were held in the molten state long enough to allow mixing of the constituents, and it has been found that about 5 to 15 minutes is sufficient for this purpose. Usually ingredients to form melts of about five to six grams each were used in proportions above set forth in detail. After the constituents had been allowed to mix, the melts were allowed to solidify and cool which was accomplished either by immediately removing heat or by controlled cooling apparatus. In certain cases the uniformity of the melt is affected by the manner in which it is cooled. These variations will be discussed later.

A specific melt in accordance with our invention was prepared as follows:

Pure GeO_2 was reduced in hydrogen at atmospheric pressure for about three hours at 650° to 700° C. Six grams of pure germanium powder so obtained were then placed in a porcelain crucible together with small flakes of pure tin amounting to 25 milligrams or about 0.8 atomic percent of tin.

The crucible and contents were then placed inside a graphite cylinder used as a heater in the high frequency field of an induction furnace, and lowered in a vertical quartz tube which was then evacuated and maintained at a pressure of about 10^{-5} mm. mercury. Power was then applied to the external coil of the induction furnace to melt the germanium and hold it molten for about 5 minutes. The melt was then allowed to cool by merely turning off the power to the coil. Thereafter wafers were cut from the alloy, and were soldered with soft-solder to a suitable metal electrode to produce a very low resistance non-rectifying contact with one face of the

wafer. The exposed face was then ground with 600 mesh alumina and etched for 2 minutes with an etching solution consisting essentially of HNO_3, HF, $Cu(NO_3)_2$ and water in proportions to be later described herein. These wafers were then assembled in suitable cartridges each provided with a conventional metal electrode or whisker which was used to contact the alloy surface. Across the rectifying contact thus produced we obtain the electrical characteristics described above.

As mentioned in the above specific example, the surfaces of these alloys are usually ground flat and then etched in a manner to be described in detail. However, as hereinafter related, the etching of the alloy surfaces is not essential since, for example, by breaking open a melt, points may be found which exhibit the aforementioned electrical rectifying characteristics. Such broken surfaces present geometrically irregular faces which introduce some difficulty in assembly of the rectifiers. Thus, grinding the alloy surface flat and etching it appears to be the most feasible manner of producing the rectifiers in the commercial practicing of our invention.

From the above Table I it will be observed that the majority of experimental work conducted in the development of our invention has been with the alloy germanium-tin. In connection with our experimental work with tin it has been found that above 0.1 atomic percent of tin content, the amount of tin added is not critical. Germanium containing above about 0.1 percent tin usually shows tin separated out, both at internal grain boundaries and on the outer surfaces. In some melts containing tin in excess of 0.1 atomic percent, ductile layers of this tin-rich material were frequently observed, particularly in the lower regions of the melt. In this connection we wish to observe that in making the germanium-tin alloys it is desirable in producing the melt that the boat or crucible in which the elements are contained be gradually removed from the hot furnace region. This will produce more uniform alloys, particularly if the melt is so removed that the top region of the melt is the last part to cool. It appears that germanium becomes saturated at about 0.1 percent tin under the melting and cooling conditions used. However, in our experimental work larger amounts of tin were added in order to observe if such solubility depended upon the amount of tin available; more tin merely segregated. At 17 atomic percent addition of tin, the entire melt was interlaced with tin-rich veins which had metallic low resistance ohmic conductivity.

With bismuth additions it is difficult to control the amount of bismuth actually remaining in the germanium during the melting cycle. A considerable fraction of the bismuth volatilizes so that quantities added have little relation to the quantities actually remaining in the melt. However, the results indicated in Table I in connection with bismuth were obtained by the addition of bismuth to the extent there indicated.

After the melts have been made as above described they are suitable for use as rectifiers of electricity by simply making contact with the surfaces of such alloys with suitable electrodes or whiskers. In most of our experimental work a 5 mil tungsten whisker sharpened electrolytically with a tip diameter of less than 0.1 mil was used as one electrode or whisker, the other electrical contact usually being made by soldering the alloy to a suitable conductor. However, tests have shown that the peak back voltages of rectifiers made from the alloys of our invention are little affected by the metal of which the whisker is made. Whiskers made of the following metals have been tried and only very slight deviations were noted over a large number of points of contact with the alloys of our invention: Mn, Pt, Ta, Ni, Fe, Zn, Mo, W, Au, Cu, Ag, Zr, Pt-Ir, and Pt-Ru. It appears therefore, that choice of a whisker material may be determined on the basis of requirements other than the peak back voltage on rectifiers using the alloys. These electrodes or whiskers may have contact with the surfaces of the alloys as formed upon solidification, or on surfaces exposed by breaking the melt. As mentioned above, however, it is desirable to grind and etch the surface. Thus in one method of producing rectifiers using the alloys of our invention, the melts, which usually were of pellet form 5 to 10 millimeters thick, may be cut into thin plates or slabs and a surface thereof ground with a suitable abrasive such as 600 mesh alumina (Al_2O_3). The abrasive used is not critical in that it has been found that other abrasives such as Cr_2O_3, MgO, Va_2O_3, SnO_2, ZnO and 4–0 paper are equally satisfactory. This may then be followed by a further grinding step with fine emery paper although this grinding step may be eliminated, if desired. without substantially altering the final product. The surface of the plate or slab is then etched with a suitable etching solution which in one modification of our invention has the following approximate composition:

4 parts by volume hydrofluoric acid (48% reagent)
4 parts by volume distilled water
2 parts by volume concentrated nitric acid
200 milligrams $Cu(NO_3)_2$ to each 10 cc. of solution.

Such a solution will satisfactorily etch the surface of the plates or slabs in about 1 to 2 minutes at room temperature and may be applied with either a swab or by immersing the surface in the solution. This etching is not particularly critical but care should be taken not to unduly extend the etching since then a high polish is produced which may impair the performance of the alloy.

We have also found that other types of etches may be used effectively on the germanium alloys of our invention in addition to the etching above described. Modified etching solutions and procedures are as follows:

A solution consisting approximately of 1 gram stannyl chloride in 50 cc. of H_2O may be used as an electrolytic bath for etching the alloy surfaces. Immersing the alloy as the anode in this solution will result in satisfactory etching within about 1½ minutes at about 2½ volts applied.

An alternative modification of an electrolytic etching solution may comprise 5 parts concentrated HNO_3 and 50 parts H_2O by volume. Using the alloy as the anode for about 1½ minutes at 1 to 2 volts will result in a satisfactory etch.

Reference may now be had to Figure 2 of the drawings illustrating the effect of etching of one of the alloys of our invention. The alloy selected to illustrate the effect of etching is identified as melt 24 P-OU136-.25Sn. This melt as appears from the aforesaid designation constitutes .25 atomic percent tin. The curve identified by reference numeral 1 illustrates the electrical characteristic of the germanium-tin alloy above identified in which the surface was ground with

600 Al_2O_3 but not etched. The curve indicated by the reference numeral 2 illustrates the electrical characteristics which were obtained on a freshly broken surface of an alloy of the above composition but which surface has not been etched. Curve member 3 illustrates the electrical characteristic of a surface ground with 600 Al_2O_3 and then etched in accordance with the manner first described.

The curve indicated by the reference numeral 4 illustrates electrical characteristics of another point on the alloy after etching as described in connection with curve 3, the curves 3 and 4 representing the best and poorest performances, respectively, of the particular germanium tin alloy above identified, after etching. It is to be observed that in this graph the voltage scale in the forward direction is there expanded by a factor of 10 as compared to the voltage scale indicating the high back voltage characteristics of the alloys of our invention. As indicated, the currents are given in milliamperes.

It will be observed from an examination of Figure 2 that the electrical characteristics of a rectifier using a broken surface exhibit high back voltages and forward conductances within the range of values obtained when using a ground and etched surface. However, such broken surfaces are shiny and geometrically irregular so that the whisker tends to skid which is undesirable in assembling permanent rectifier units. From Figure 2 it is apparent that the high back voltage and high back resistance properties are inherent in the alloys and that the etching is effective for restoring such properties after grinding. Further, we have discovered that natural surfaces formed when solidifying the alloys in vacuum will, if not contaminated or otherwise affected by grinding, give high back voltages and high back resistances when mounted and tested in air.

For certain applications of these rectifiers it is desirable that they have back resistances exceeding one megohm at about 5 volts. Using the procedure described above will occasionally produce such high back resistances. However, we have found that a substantial and permanent increase in the back resistance can be effected by applying power overloads across the contact, for short intervals of time, each of length about ¼ to 1 second or longer. The power treatment can be effected with the use of either alternating or direct current. By gradually increasing the voltage applied, and hence the current passed by the contact during successive pulses, an optimum value can be found to produce the maximum back resistance for a given contact. For direct current treatment in the forward direction such optimum current values range from about 200 to 800 milliamperes. For alternating power treatment the optimum values of forward peak current range from about 300 milliamperes to 1000 milliamperes. One can apply such alternating current treatment simply by connecting the rectifier in series with a current limiting resistance and the secondary of a transformer. Depending upon the size of this current limiting resistance, values of 10 to 40 ohms have been used, voltage pulses ranging from 7 to 60 volts across the rectifier and resistance serve to yield the maximum increase in back resistance.

Table III shows the permanent effects of such power treatment upon a few typical rectifiers using alloys of our invention and prepared as described. It will be seen from the table that the most significant effect of the power treatment is the increase in the back resistance as measured at about 4.5 volts. This resistance is increased by factors ranging from about 10 to 50 times the values measured before treatment. Relatively minor increases of 10 to 20 per cent are effected on the peak back voltage. Forward currents at one volt are in general decreased by amounts ranging from 10 to 50 per cent.

TABLE III

Effects of power treatment

[Values before power treatment are followed in brackets by values after power treatment.]

Alloy used in Rectifier	Peak Back Voltage (volts)	Forward Current at one volt (milliamperes)	Back Resistance at 4.5 volts (megohms)
24L-.50 Sn	75 (105)	9 (4.5)	0.02 (3)
24L-.50 Sn	100 (140)	11 (6.5)	.30 (4)
24P-.25 Sn	95 (115)	13 (7)	.25 (2.5)
22W$_5$-1.0 Sn	80 (95)	6 (6)	.15 (8)
22W$_5$-1.0 Sn	100 (120)	8 (8)	.05 (0.8)
24Q-.40 Sn	90 (115)	24 (10)	.04 (7.5)
24Q-.40 Sn	90 (110)	20 (17)	.48 (15)
24Q-.40 Sn	150 (175)	40 (10)	.20 (4)
27A-N_2	90 (95)	10 (8)	.20 (1)
27A-N_2	100 (120)	15 (10.5)	.13 (2)
27A-N_2	80 (105)	18 (10)	.10 (4)
27B-N_2	130 (150)	4 (4)	.40 (2)
27B-N_2	95 (115)	10 (6)	.20 (3)
27E-N_2	95 (105)	10 (6.4)	.40 (7.5)
27E-N_2	110 (120)	15 (10)	.20 (3)
28D-N_2	90 (95)	14 (8)	.38 (2.5)
29U-N_2	40 (45)	30 (16)	.81 (3.9)
29U-N_2	80 (95)	16 (10)	1.0 (7.5)

It has been demonstrated above that the high back voltage, high back resistance, and good forward conductance properties disclosed are inherent in the germanium alloys of our invention. Modifications of surface treatments or power treatments as described above will, however, vary the magnitude of these properties within certain general limits. For example, on a given alloy surface, variations in surface treatment and power treatment may be expected to vary the average peak back voltage by a factor of about 2, the average forward current by a factor of about 2, and the average back resistance by factors up to 50. It will be noted that the back resistance is the property most sensitive to variations in treatment, particularly to power treatment.

The following Table IV summarizes, on the basis of all melts made in experimental work conducted under our invention, the approximate figures of the minimum, average, and maximum values of peak back voltage and forward current at one volt which might be expected on the germanium alloys consisting of the addition of a single element.

TABLE IV

Alloy	Peak Back Voltage (volts)			Forward Current at one volt (milliamperes)		
	Min.	Ave.	Max.	Min.	Ave.	Max.
Ge-Sn	25	75	150	2	15	30
Ge-N_2	20	80	160	7	10	25
Ge-Ca	25	75	150	5	15	25
Ge-Sr	25	75	150	5	10	25
Ge-Ni	20	50	90	7	15	30
Ge-Zn	25	50	100	5	12	20
Ge-Pb	25	70	135	1	15	25
Ge-Pd	30	65	110	5	15	25
Ge-Mg	10	50	100	2	10	20
Ge-Cd	20	50	105	5	12	15
Ge-Ba	15	50	125	7	13	20
Ge-Bi	15	40	100	10	15	30
Ge-Ag	25	40	80	7	10	20
Ge-Tl	10	30	70	3	7	15
Ge-Co	20	30	35	10	15	20
Ge-Ta	20	40	70	3	15	30
Ge-Cu	15	40	75	1	5	40
Ge-Cb	15	25	40	5	15	40
Ge-V	10	25	65	10	25	40
Ge-U	20	25	50	2	5	20
Ge-Cr	5	15	25	5	15	25

It will appear from the above table that the ranges of values for the better alloys appear to be quite similar. Differences enter in the manner in which the values, within the ranges indicated, are concentrated. For example, the nitrogen alloys can usually be expected to have 70 to 90 percent of back peak voltages over 60 volts. Values on the melts are more uniformly spread within the range of the limits given above. For the tin melts approximately 50% of the points on the surfaces thereof will have voltages above 60 volts. It appears that the pure germanium alloyed with tin or melted in an atmosphere of nitrogen represents the most advantageous alloy. Following them, alloys of pure germanium with calcium, strontium or nickel appear to be in order. It is to be understood, however, that one skilled in the art working within the range of the alloys herein disclosed will readily be able to produce alloys having high back voltage and resistance characteristics and good forward conductances.

In Figure 3 of the drawings we have shown one type of rectifier in which our invention may be embodied. In the form of the device there shown a wafer **5** which may be of any of the germanium alloys above disclosed is mounted to have a low resistance non-rectifying contact with a metal electrode member **6**. An electrode or whisker **7** is connected at one end to an electrode supporting member **8** with the end of the whisker in contact with the surface of the germanium alloy wafer **5**. The standard **9** provides for mounting of the members supporting the wafer **5** and electrode or whisker **7** in insulated relation. The rectifier contemplated by our invention may be of various forms, the only critical constructional feature being that the germanium alloy wafer comprising the semiconductor, and the whisker for contacting the surface of the wafer being arranged and supported so that one end of the whisker engages the semi-conductor surface. It is understood that suitable leads are connected to the wafer or semi-conductor and to the whisker or metal electrode so that the device may have application in any desired circuit for use in the rectification of current.

While we have disclosed what we consider to be the preferred embodiments of our invention, it will be understood that various modifications may be made therein without departing from the spirit and scope of our invention.

We claim:

1. An electrical device comprising a semi-conductor, a counter electrode having substantially point contact with said semi-conductor and a second electrode having an area of contact with said semi-conductor which is large compared to that of the counter electrode, said semi-conductor consisting of germanium of the order of 99% purity in combination with at least one of the elements from the group consisting of magnesium, calcium, zinc, strontium, cadmium, and barium, said device having a peak back voltage in the range in excess of 10 volts and approaching the order of 200 volts.

2. An electrical device comprising an alloy formed of a mixture of germanium having a purity of the order of 99% and calcium in an amount of between 0.28 and 2.0 atomic percent, and a pair of electrode elements in contact with said formed alloy, one of said electrode elements having substantially point contact with said alloy and the second of said electrodes having an area of contact which is large compared to that of the point contact electrode.

3. An electrical device comprising an alloy formed of a mixture of germanium having a purity of the order of 99% and strontium in an amount of between 0.5 and 1.0 atomic percent, and a pair of electrode elements in contact with said formed alloy, one of said electrode elements having substantially point contact with said alloy and the second of said electrodes having an area of contact which is large compared to that of the point contact electrode.

4. An electrical device comprising an alloy formed of a mixture of germanium having a purity of the order of 99% and barium in an amount of between 0.4 and 0.5 atomic percent, and a pair of electrode elements in contact with said formed alloy, one of said electrode elements having substantially point contact with said alloy and the second of said electrodes having an area of contact which is large compared to that of the point contact electrode.

5. The method of making an electrical device which comprises mixing germanium having a purity of the order of 99% with at least one of the elements from the class consisting of magnesium, calcium, zinc, strontium, cadmium, and barium, applying heat to the mixture to reduce the mixture to a fluid state, maintaining the heat for a time period sufficiently long to permit mixing of the selected constituents, removing the heat to permit solidification of the mixture, cutting from the ingot formed upon mass solidification wafers to which contact electrodes may be applied, and applying contact electrodes to said wafers.

6. The method of claim 5, including the additional steps of grinding the severed wafers and then etching the ground surfaces to provide optimum contact points for said contacting electrode members.

7. The method of claim 5, including, in addition, the step of etching a surface of a wafer cut from the ingot before applying a contact electrode.

8. The method of claim 5, including, in addition, the step of etching a surface of a wafer cut from the ingot in a solution made up of approximately 4 parts by volume of hydrofluoric acid (48% reagent), 4 parts by volume of distilled water, 2 parts by volume of concentrated nitric acid, and 200 milligrams $Cu(NO_3)_2$ to each 10 cc. of solution for a time period in the general range of between 1 and 2 minutes.

9. The method of claim 5, including securing one of said electrodes to one surface of a cut wafer, locating a second substantially point contact electrode upon a different surface of the cut wafer and in substantially point contact therewith, and then applying electric power between the electrodes and the wafer.

10. The method of claim 9, including, in addition, regulating the supplied current in the forward direction through the cut wafer and limiting the current value to the range between 200 and 800 milliamperes applied in pulses of between ¼ to 1 second in length.

11. The method of claim 10, including, in addition, the steps of connecting the formed device in series with a current limiting resistance and a secondary of a transformer of alternating electric currents controlling the peak current in the forward direction to the order of between 300 and 1000 milliamperes so that the voltage across the device and limiting resistance is of the order of

between 7 and 60 volts and the limiting resistance is of the order of 10 to 40 ohms and regulating the period of application of the alternating current to intervals varying between ¼ and 1 second in time duration.

12. The method of claim 5, including electrolytically etching one of said wafers as an anode in a solution in the proportions of approximately 1 gram stannyl chloride to 50 cc. water for about 1½ minutes at about 2½ volts.

13. The method of claim 5, including electrolytically etching one of said wafers as an anode in a solution in the proportions of approximately 5 parts concentrated nitric acid to 50 parts water by volume for about 1½ minutes at about 1 to 2 volts.

14. An electrical device comprising a semiconductor, a counter electrode having substantially point contact with said semi-conductor and a second electrode having an area of contact with said semi-conductor which is large compared to that of the counter electrode, said semi-conductor consisting of germanium of the order of 99% purity in combination with at least one of the elements from the class consisting of magnesium, calcium, zinc, strontium, cadmium, and barium, said device having a peak back voltage in the range in excess of 10 volts and approaching the

order of 200 volts, the back resistance of said device being in the order of between 10,000 ohms to several megohms at about 5 volts and the forward current being in the range of between 5 and 40 milliamperes at 1 volt in the low resistance direction of current flow through the device.

15. An electrical device comprising a body of semi-conducting material consisting essentially of germanium of the order of 99% purity in combination with at least one element from the group consisting of magnesium, calcium, zinc, strontium, cadmium, and barium, and two electrodes in electrical contact with said body.

KARL LARK-HOROVITZ.
RANDALL M. WHALEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,530,110	Woodyard	Nov. 14, 1950

OTHER REFERENCES

Merrit, Proc. Nat'l. Acad. Science, vol. 11, 1925, pages 743–748.