June 7, 1955 R. K. WILLARDSON ET AL 2,710,253

SEMICONDUCTING ALLOY

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Fig 1

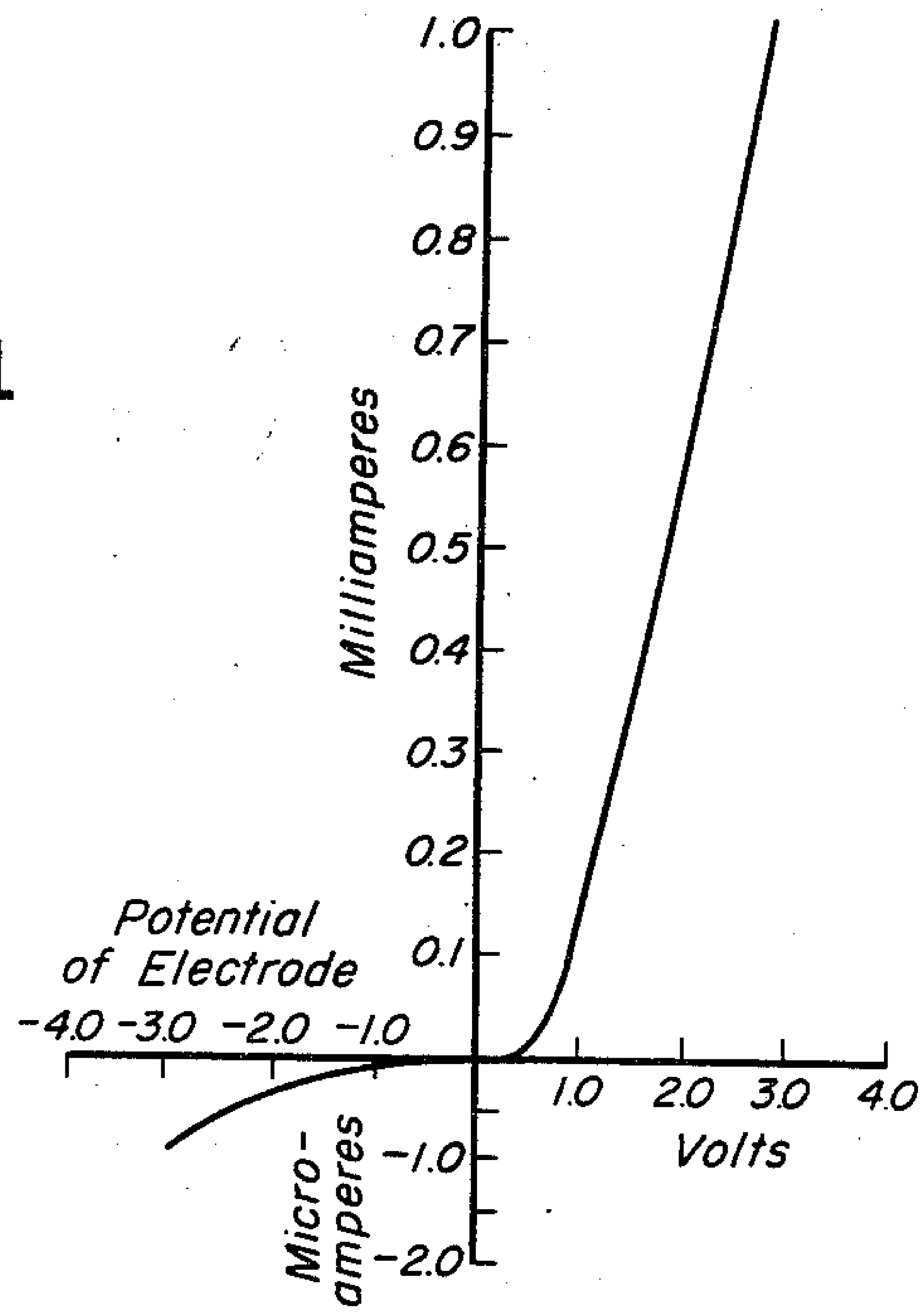

Fig 2

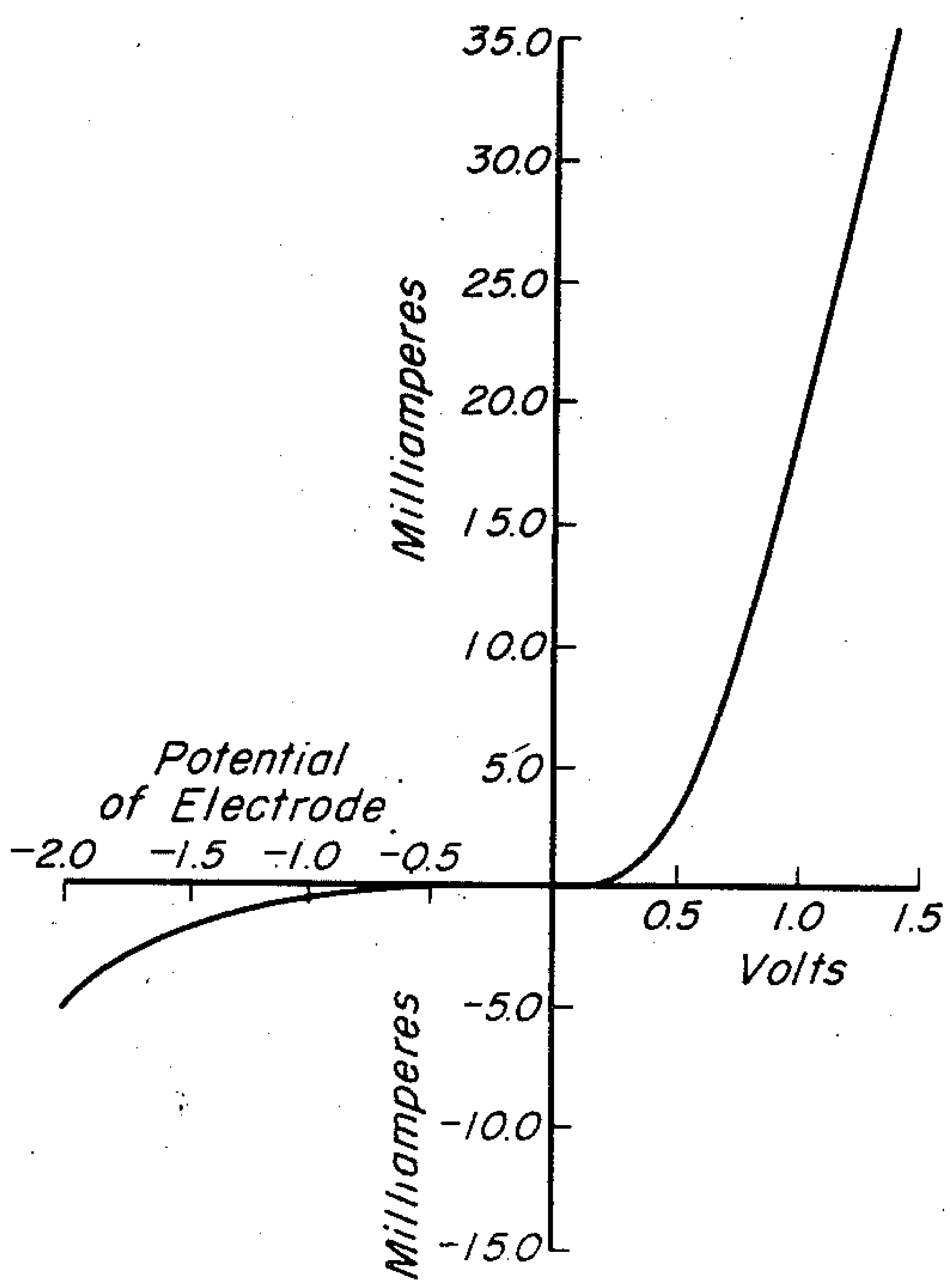

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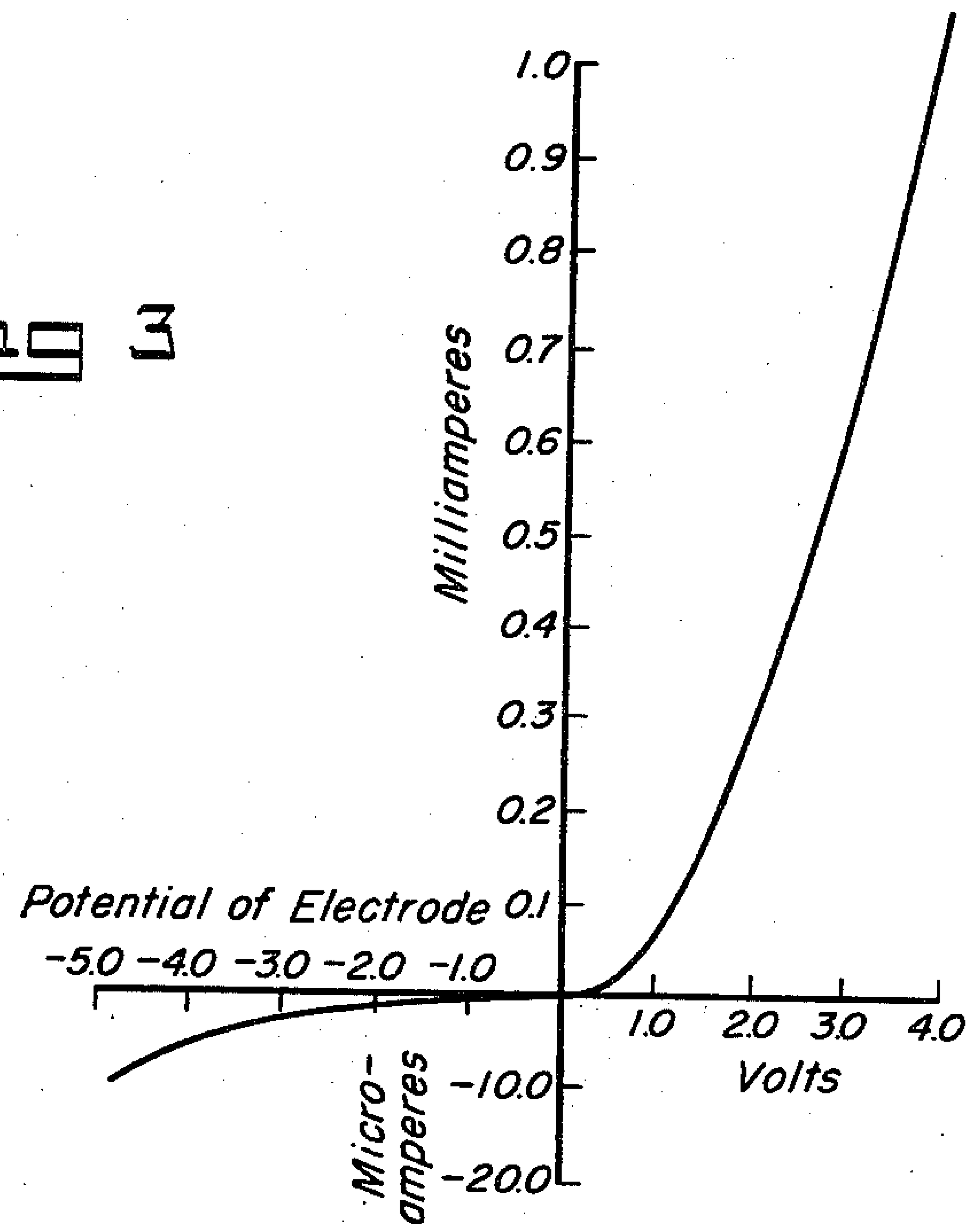
Fig 3



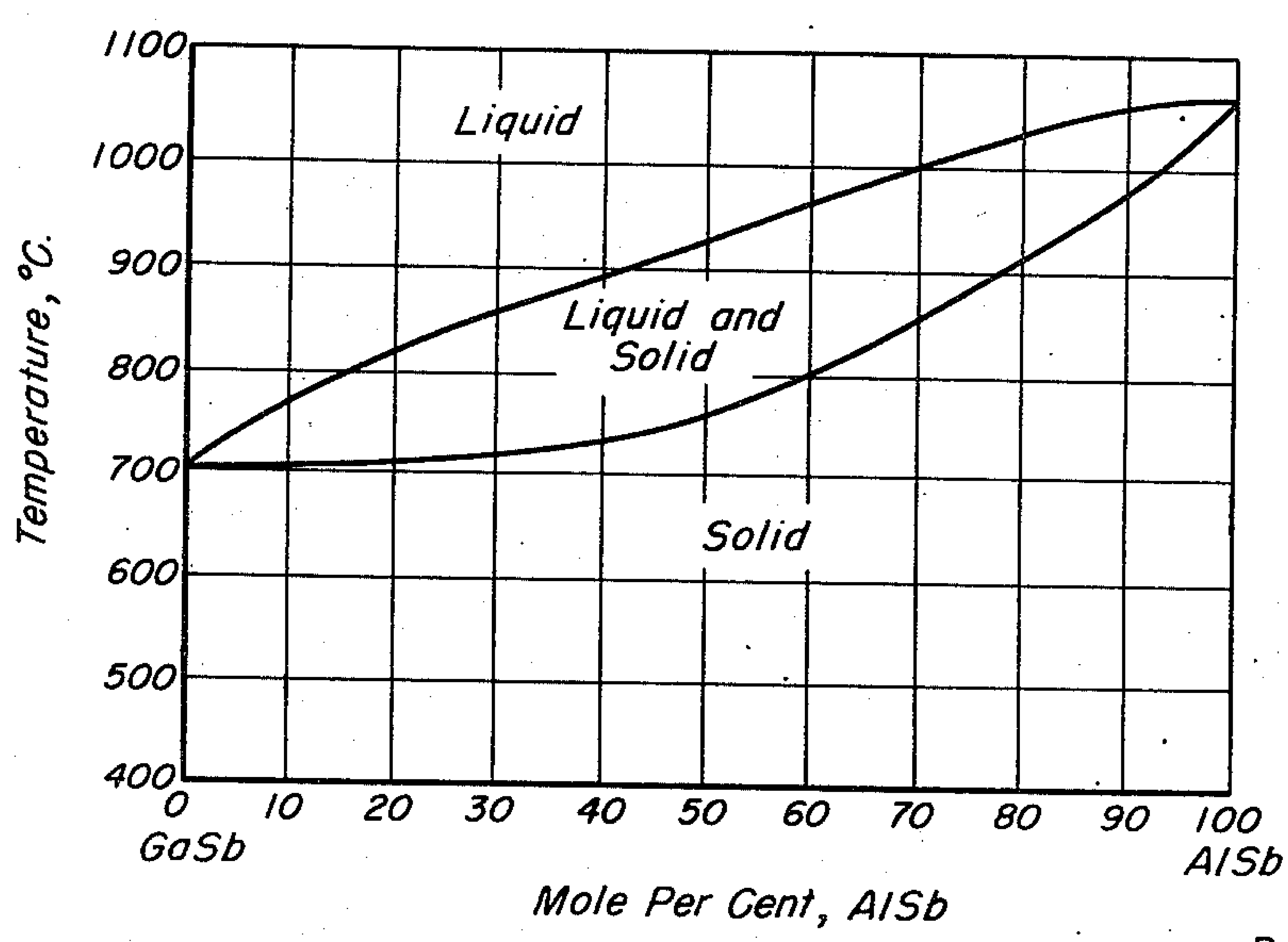


Fig 4

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SEMICONDUCTING ALLOY

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Application October 19, 1953, Serial No. 386,878

9 Claims. (Cl. 75—149)

This invention relates to alloy compositions of aluminum antimonide and gallium antimonide.

In the past, germanium and silicon have found wide application as semiconductor materials in transistors and rectifiers. Germanium has a band separation of about 0.75 electron volt, an electron mobility of about 3,600 cm.^{2} per volt sec., and a melting point of 936° C. Silicon has a band separation of about 1.15 electron volts, an electron mobility of about 1,200 cm.^{2} per volt sec., and a melting point of 1420° C. Thus, while these two materials are extremely useful in such applications, there are certain inherent limitations presented. Because of its low-energy band separation, germanium is useful as an asymmetric conductor only at temperatures below 70° C. Silicon, on the other hand, is useful at higher temperatures, but its high melting point introduces difficulties in fabrication.

It has been shown that aluminum antimonide and gallium antimonide are semiconducting compounds and are suitable for use in various applications requiring asymmetric conduction, such as in rectifiers and transistors. R. K. Willardson, A. C. Beer, and A. E. Middleton, "Electrical Properties of Semiconducting AlSb" (presented at the Spring Meeting of the Electrochemical Society, April 12–16, 1953); also, H. Welker, Zeitschrift fur Naturforschung, vol. 8A, April, 1953, and copending U. S. patent application No. 336,298, filed February 11, 1953, by R. K. Willardson, A. C. Beer, and A. E. Middleton. Aluminum antimonide has a band separation of about 1.6 electron volts, a melting point of about 1050° C., and a carrier mobility of at least 100 cm.^{2} per volt sec. for p-type and n-type carriers in polycrystalline material. Gallium antimonide has a band separation of 0.7 electron volt, a carrier mobility up to 2,000 cm.^{2} per volt sec. in polycrystalline material and a melting point of 702° C. It is noted that the band separation of aluminum antimonide is much higher than that of either germanium or silicon, while the melting point is less than that of silicon. This shows that aluminum antimonide is useful at higher temperatures, yet does not have the fabrication limitations of silicon. The mobility of electrons in aluminum antimonide, however, is not as high as that of silicon or germanium. On the other hand, electrons in gallium antimonide have a mobility between that for electrons in silicon and germanium but its band separation is less than that of germanium. Thus, the use of gallium antimonide as a semiconductor is limited.

It has been found as a part of the present invention, however, that if a solid solution of aluminum antimonide and gallium antimonide be prepared from the appropriate proportions of each compound then the band separation of the resulting alloy composition will, in general, lie between those of the two constituent compounds. It has been found also that valuable improvements in the physical and chemical stability, such as resistance to oxidation or deterioration in humid environments, can be engendered in the resulting alloy composition as compared with pure aluminum antimonide.

It is an object of this invention to provide a semiconducting material composed primarily of aluminum antimonide and gallium antimonide.

Another object of this invention is to provide a semiconducting material with improved energy band separation or ease of preparation over silicon or germanium.

Another object of this invention is to provide a semiconducting material having better carrier mobility and corrosion resistance than aluminum antimonide.

Still another object of this invention is to provide a semiconducting material with increased resistance to corrosion by water and oxygen.

A further object of this invention is to provide an improved semiconductor material useful at high temperatures.

A still further object of this invention is to provide a high-temperature semiconducting material that may be formed at temperatures less than 1100° C.

Further objects of this invention will become apparent from the included drawings, the following specification, and the appended claims.

In the drawings:

Fig. 1 is a graph illustrating a representative voltage-current characteristic curve of a medium forward resistance N-type rectifier, the semiconductor consisting of about 71.6% by weight of antimony, 20.5% by weight of gallium, and 7.9% by weight of aluminum, and having a Phosphor-bronze point contact electrode.

Fig. 2 is a graph illustrating representative voltage-current characteristic curve of a low forward resistance N-type rectifier, the semiconductor consisting of about 71.6% by weight of antimony, 20.5% by weight of gallium, and 7.9% by weight of aluminum, and having a Phosphor-bronze point contact electrode.

Fig. 3 is a graph illustrating a representative voltage-current characteristic curve of an N-type rectifier, the semiconductor consisting of about 71.6% by weight of antimony, 20.5% by weight of gallium, and 7.9% by weight of aluminum, and having a tungsten point contact.

Fig. 4 is a phase diagram illustrating the melting temperatures and solidification temperatures of the aluminum antimonide, gallium antimonide system.

Pure aluminum antimonide decomposes to a black, amorphous powder, even in one to two days after its production (Zeitschrift fur Anorganische und Allgemeine Chemie. G. Tammann and A. Ruhenbeck, vol. 223, 1935, p. 288). It has been found that this decomposition may be reduced or entirely eliminated by additions of two mole per cent or greater of gallium antimonide to the aluminum antimonide. It has also been found that additions of from two mole per cent to twenty mole per cent of gallium antimonide to aluminum antimonide, while providing this greatly improved corrosion resistance, do not substantially affect the electrical characteristics of the semiconductor.

Additions of greater than twenty mole per cent of gallium antimonide to aluminum antimonide have been found to increase the mobility of the semiconductor. As an example, a semiconductor containing 50 mole per cent gallium antimonide, balance aluminum antimonide, has a mobility of about 1000 cm.^{2} per volt sec. in polycrystalline material. The band separation of this sample is about 1.1 ev. It is seen that this material has a much higher mobility than a polycrystalline aluminum antimonide, while having a higher band separation than gallium antimonide. Although the electron mobility in this alloy is somewhat less than that for germanium, its band separation is higher than that of germanium, and it would thus be useable at a higher temperature. In order for the electrical characteristics of the semiconductor of this invention to be substantially different from those of gallium antimonide, the semiconductor should contain at least five atomic per cent aluminum.

From Fig. 4, it is seen that the melting temperature of the alloy of this invention is less than that of aluminum antimonide, and from this standpoint the alloy is thus more easily fabricated than either aluminum antimonide or silicon. It has been found that a semiconductor containing about 25 atomic per cent antimony has a band separation and carrier mobility about the same as that of silicon, while not having the high melting point of silicon.

For fabrication of the alloy of this invention, it may be more convenient to express the composition of the semiconductor in terms of weight percentages rather than atomic percentages. In this case, the basic expression for the composition may be stated as follows: the sum of the weight percentage of gallium plus 2.01 times the weight percentage of aluminum is equal to about 36.4. This expression is modified by the limitation that a material having substantially the same electrical characteristics as aluminum antimonide while having improved corrosion characteristics has a gallium content of from 8.85% to 0.93%, an aluminum content of from 13.72% to 17.65%, and balance antimony, while a material having substantially greater carrier mobility as well as greater corrosion resistance than aluminum antimonide has a gallium content of from 33.5 to 8.85 per cent, an aluminum content of from 1.44% to 13.72% and balance antimony. Within these ranges of constituents, the alloy of this invention has been found to exhibit rectifier and transistor properties suitable for most applications of the semiconductor. Figs. 1, 2, and 3 illustrate typical voltage-current characteristics of an alloy containing 20.5% by weight of gallium and 7.9% by weight of aluminum, balance antimony.

These compositions are produced by either of two methods. The compounds aluminum antimonide and gallium antimonide in the desired proportion may be mixed together at an appropriate temperature, but this method introduces difficulty because of the differences in melting point of the materials. A preferred method of fabrication involves reacting the aluminum, the antimony, and the gallium together. The proportions of aluminum and gallium used determine the final characteristics of the material. A small amount of aluminum present in the composition serves to increase the band separation while reducing the mobility of the charge carriers slightly. Larger amounts of aluminum, while increasing the band separation, cause a further decrease in the mobility of the charge carriers in the compound. Even with the mobility decreased materially, however, the resulting composition has valuable semiconducting properties. It is noted that the melting point of gallium antimonide is only 702° C. as compared with 1050° C. for aluminum antimonide. When fusing these two compounds together, it has been found that, unless agitation is provided, most of the aluminum antimonide will rise to the top of the solution and, thus, not mix properly with the gallium antimonide. This difficulty is not so great when reacting the three elements together. The alloy composition of this invention can be prepared by reacting the constituents in a crucible of graphite or any other material that will not react appreciably with the aluminum, gallium, or antimony, or with the compounds of gallium antimonide and aluminum antimonide.

As is the case with germanium and silicon, various impurities may be added to the alloy to control the conductivity type of the semiconductor. These impurities are added to the alloy during the preparation. Thus, zinc antimonide, cadmium antimonide, or similar compounds may be added to obtain a P-type semiconductor, and gallium telluride, gallium selenide, gallium sulfide, or similar compounds may be added to obtain an N-type semiconductor. It is preferred that the impurity content be no greater than 0.01 atomic per cent. Control of the conductivity may also be obtained, as in other semiconductors, by neutron bombardment and electroforming.

The contacts for devices utilizing the semiconductor of this invention may be other semiconductors or metals. In the case of a rectifier either point contacts (for example Phosphor bronze points) or deposited metallic contacts may be used. By control of impurities, barrier layers (junctions) may also be formed in the alloy.

Although the alloy composition has been described with particular reference to its use in rectifiers and transistors, it is also contemplated that it may be used in other applications, since it has been found to exhibit thermoelectric and photoelectric properties as well as asymmetric conduction and transistor properties.

It will be understood, of course, that the words used herein are words of description rather than of limitation, and that various changes may be substituted without departing from the scope of the invention herein disclosed.

What is claimed is:

1. A semiconducting material consisting essentially of from 33.5% to 0.93% by weight of gallium, from 1.44% to 17.65% by weight of aluminum, balance antimony, in which the sum of the weight percentage of gallium and 2.01 times the weight percentage of aluminum is equal to about 36.4.

2. A semiconducting material consisting essentially of from 33.5% to 0.93% by weight of gallium, from 1.44% to 17.65% by weight of aluminum, balance antimony, in which the sum of the weight percentage of gallium and 2.01 times the weight percentage of aluminum is equal to about 36.4, and characterized by better corrosion resistance than aluminum antimonide.

3. A semiconducting material consisting essentially of from 33.5% to 0.93% by weight of gallium, from 1.44% to 17.65% by weight of aluminum, balance antimony, in which the sum of the weight percentage of gallium and 2.01 times the weight percentage of aluminum is equal to about 36.4, having rectifier characteristics and being useable as a transistor material, and characterized by better corrosion resistance than aluminum antimonide.

4. A semiconducting material consisting of from 33.5% to 8.85% by weight of gallium, from 1.44% to 13.7% by weight of aluminum, balance antimony, in which the sum of the weight percentage of gallium and 2.01 times the weight percentage of aluminum is equal to about 36.4.

5. A semiconducting material consisting essentially of from 33.5% to 8.85% by weight of gallium, from 1.44% to 13.7% by weight of aluminum, balance antimony, in which the sum of the weight percentage of gallium and 2.01 times the weight percentage of aluminum is equal to about 36.4, and characterized by a higher carrier mobility, a lower melting point, and greater corrosion resistance than aluminum antimonide.

6. A semiconducting material consisting essentially of from 33.5% to 8.85% by weight of gallium, from 1.44% to 13.7% by weight of aluminum, balance antimony, in which the sum of the weight percentage of gallium and 2.01 times the weight percentage of aluminum is equal to about 36.4, having rectifier characteristics and being useable as a transistor material, and being characterized by a higher carrier mobility, a lower melting point, and greater corrosion resistance than aluminum antimonide.

7. A semiconducting material consisting of from 8.85% to 0.93% by weight of gallium, from 13.7% to 17.65% by weight of aluminum, balance antimony, in which the

sum of the weight percentage of gallium and 2.01 times the weight percentage of aluminum is equal to about 36.4.

8. A semiconducting material consisting of from 8.85% to 0.93% by weight of gallium, from 13.7% to 17.65% by weight of aluminum, balance antimony, in which the sum of the weight percentage of gallium and 2.01 times the weight percentage of aluminum is equal to about 36.4, and characterized by greater corrosion resistance than aluminum antimonide.

9. A semiconducting material consisting of from 8.85% to 0.93% by weight of gallium, from 13.7% to 17.65% by weight of aluminum, balance antimony, in which the sum of the weight percentage of gallium and 2.01 times the weight percentage of aluminum is equal to about 36.4, having rectifier characteristics and being useable as a transistor material, and characterized by greater corrosion resistance than aluminum antimonide.

No references cited.