

[54] **VOLTAGE-DEPENDENT RESISTORS**

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[22] Filed: **Jan. 26, 1970**

[21] Appl. No.: **5,738**

[30] **Foreign Application Priority Data**

Jan. 31, 1969 Netherlands.....6901538

[52] U.S. Cl.**317/234 R, 317/234 S, 317/235 UA, 117/212, 338/223, 338/228, 338/327, 338/226**

[51] Int. Cl.**H011 9/00, H011 9/06**

[58] Field of Search**317/234, 235; 338/223, 228, 338/327, 226, 239; 117/212, 200; 29/610**

[56]

References Cited

UNITED STATES PATENTS

3,210,831 10/1965 Johnson et al.29/155.71

3,560,812 2/1971 Hall et al.317/235

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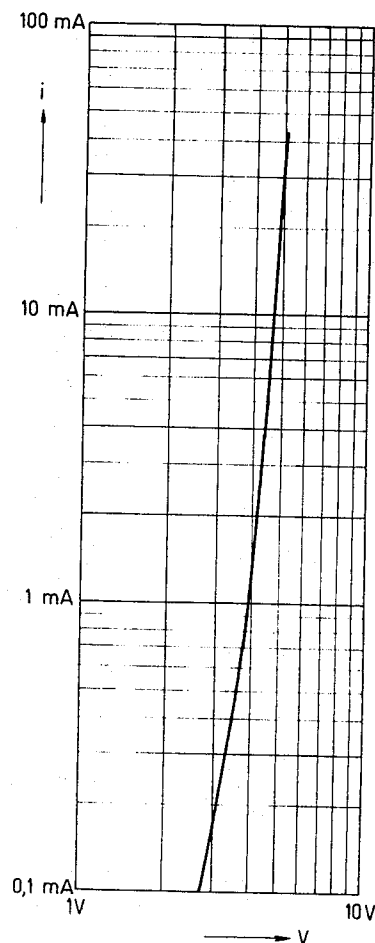
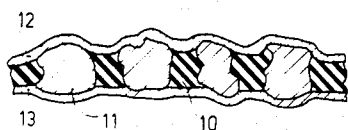
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[57]

ABSTRACT

Voltage-dependent resistor comprising a foil of insulating material in which semiconductor grains are embedded, which project from the foil on both sides and are in contact with electrode layers applied to both sides of the foil, the grains having a diameter of not more than $150\ \mu$ and consist of a III-V compound, preferably GaP having an energy gap of at least 1.1 eV.

2 Claims, 3 Drawing Figures



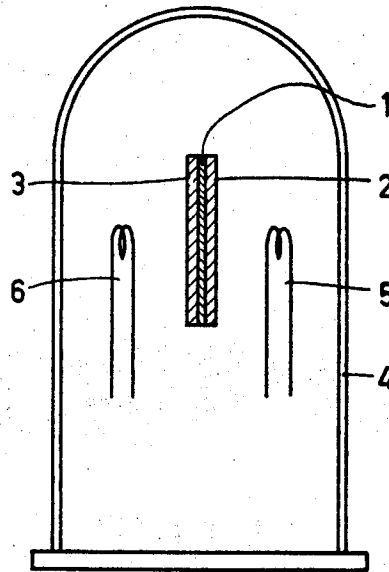


fig. 1

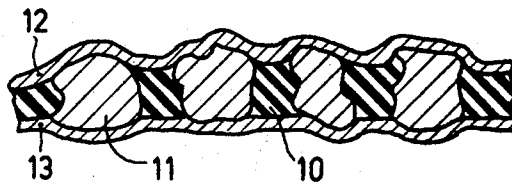


fig. 2

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PATENTED JUN 13 1972

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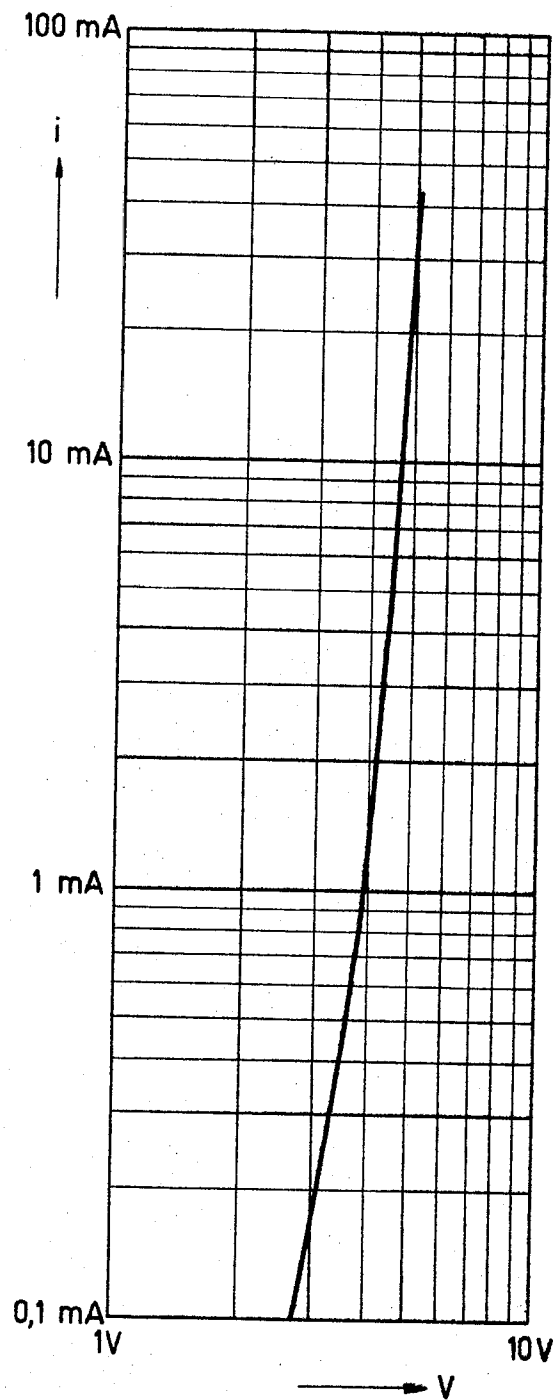


fig. 3

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VOLTAGE-DEPENDENT RESISTORS

The invention relates to voltage-dependent resistors consisting of elements of semiconductor material provided with two rectifying metal-semiconductor contacts (Schottky barriers) or with such a rectifying and an ohmic contact.

These non-linear resistors are constructed as diodes. They are, however, employed in a region of operating voltage in which as a result of tunnel effect and/or avalanche effect the barriers pass in the reverse direction a current increasing non-linearly with voltage.

Resistors of this kind are known, for example, from the Austrian Pat. Specification No. 265,370.

Non-linear resistors are furthermore constructed from a plurality of active semiconductor elements known from U.S. Pat. No. 3,210,831. These composite resistors are formed by a foil of insulating material in which grains of semiconductor material are included so that they project freely from both surfaces. The two surfaces of this foil are coated with metal contact layers which interconnect electrically projecting parts of grains.

The author of said U.S. Pat. Specification ascribes the non-linearity of the resistors of this construction to a property, i.e., the voltage-dependence of the resistance of the semiconductor materials used by him, among which only silicon carbide is specifically mentioned in said Specification.

As a matter of course the resistance of semiconductor material will only be dependent upon voltage if it is prepared in a special manner, for example, by introducing pn-junctions. However, in said U.S. Pat. Specification it is not indicated in any way how the non-linearity of the resistance material which is said to produce the desired voltage-dependence of the resistor, is obtained. Probably it has to be assumed that also in the composite resistors disclosed in the U.S. Pat. No. 3,210,831 the non-linearity is produced by barriers as is the case with the simple voltage-dependent resistors, disclosed in the Austrian Pat. Specification No. 265,370.

However that may be, it is obvious that the construction of the resistors according to U.S. Pat. No. 3,210,831 has the advantage that as compared with those described in Austrian Pat. Specification No. 265,370 the resistors can be made in a simpler manner and by using comparatively small quantities of semiconductor material.

On the other hand, as stated in Austrian Pat. Specification No. 265,370 semiconductor elements consisting of gallium arsenide or indium phosphide, that is to say, a 3-5 compound having an energy gap of more than 1.1 eV are particularly suitable for the construction of voltage-dependent resistors.

Object of the invention is to provide voltage-dependent resistors having a strong non-linearity particularly suitable for use at low operational voltages, for example, lower than 10 V.

The invention relates to a voltage-dependent resistor consisting of an uninterrupted foil of electrically insulating material in which semiconductor grains are included so that they freely project from both surfaces, said foil being coated on both surfaces with metal contact layers which electrically interconnect protruding parts of grains and is characterized in that the grains consist of a semiconductor 3-5 compound having an energy gap of more than 1.1 eV and have a size of 150μ at the most and in that at least one of the contact layers with the protruding grain parts forms metal-semiconductor barriers.

Like those of Austrian Pat. Specification No. 265,370, resistors of this construction have a particularly great non-linearity, but they exhibit the same also with markedly lower operational voltages than mentioned in said Patent Specification.

By using semiconductor grains of not more than 150μ and a great grain density on the foil, even with a small size of the foil surface, it is moreover possible to make the resistors with reliable reproducibility of the resistance properties owing to the great number of elements of which said resistors consist.

The resistivity of the semiconductor grains may be adjusted in known manner by the addition of donors and acceptors.

Apart from parameters such as the surfaces of the contact layers, the grain density of the foil and the size and composition of the grains this measure provides the possibility of adjusting the desired operational voltage of the resistors.

Although various 3-5 compounds having an energy gap of more than 1.1 eV may be used such as GaAs, InP, AlSb, AlP, AlAs, it has been found that resistors having particularly advantageous properties, i.e., a high non-linearity at a low voltage are obtained on the basis of semiconductor grains of gallium phosphide as will be illustrated in the following example.

Foils including grains of semiconductor material in the form of a one-grain thick layer may be made, as is known, in various ways.

The grains may be spread on a substrate and subsequently embedded in a film of liquid synthetic resin or pressed into a synthetic resin foil, if necessary, whilst heated. Subsequently the grain surfaces are locally freed of the insulating synthetic resin, for example, by grinding, dissolving or etching so that contact layers can be applied. With these methods it is of course not easy to obtain foils in which the grains are arranged in one-grain thick layer with great uniform density.

For the manufacture of the resistors in accordance with the invention it is therefore preferred to use a method, otherwise also known for example in U.S. Pat. 3,522,339, in which an adhesive layer for example, of a rubber glue, is applied to a substrate, on which the grains are spread. After the removal of the grains not adhering to the adhesive layer a uniform layer of great density with a thickness of one grain is obtained.

Further advantages of this method are that after embedding the grains in a film of an insulating synthetic resin the formed foils can easily be removed from the substrate and that, moreover, by simply washing off the adhesive layer the grains protrude freely on this side of the foils and may be provided with the required contact layer. The grain surfaces on the other side of the foil may be freed for contact application by dissolving or etching.

For the composition of the foils all kinds of thermoplastic and thermo-hardening materials of good electrical insulation properties may be employed. It is, however, preferred to use polyesters and particularly polyurethanes which exhibit, apart from good mechanical and insulating properties, a great preservability.

In order to obtain advantageous and reproducible resistance properties it is of course important to start from semiconductor substances of high purity.

The contact layers may be applied by vapor-deposition, if desired, in an electric field (sputtering). It is known to use a plurality of metals, for example, gold, platinum, silver, copper and aluminum for the formation of metal-semiconductor barriers.

The output of voltage-dependent resistors of good quality may be materially improved by some measures in the manufacture.

It has been found that by ion bombardment on the foil surfaces in a gas discharge prior to the application of the contact layers resistors can be obtained which exhibit a strongly reduced noise.

It has furthermore been found that "formation" of the contacted resistance foil by means of a current pulse has a favorable effect. Presumably, bad places in the resistors, for example, due to the formation of ohmic contacts on a few semiconductor grains are burnt off by the current pulse.

Although it is possible, to provide the resistance foil with one rectifying contact layer and one ohmic contact layer, it is frequently preferred to provide the resistors on both sides with rectifying contact layers because the unilateral application of ohmic contact layers renders the manufacture more difficult.

The invention will now be described in greater detail with reference to the accompanying drawing in which:

FIG. 1 is a schematic view of an apparatus for carrying out the method of the invention;

FIG. 2 is a cross-sectional view of a resistor of the invention; and

FIG. 3 is a characteristic curve of a resistor of the invention.

Resistors according to the invention may be manufactured as follows.

The starting material is a powder of pure gallium phosphide with a zinc addition of 5 ppm so that the powder is p-conductive and has a resistivity of 0.3 Ohm.cm. at 20° C. A fraction of a granular size of 40 to 60 μ is sieved out.

A layer of a rubber glue is applied to a glass substrate and the grains of gallium phosphide are uniformly spread thereon. After drying at a slightly higher temperature the non-adhering grains are removed by means of a soft brush.

The substrate with the adhering grains is then dipped in a solution of polyurethane-forming compounds. After dripping off the layer is dried in air and heated at 150° C. in an air stream for three-fourths hour for partial curing of the polyurethane.

The foil is then removed from the glass substrate and the glue layer present on one side is removed by rinsing in a mixture of xylene and petrol. The foil is then carefully washed in order of succession with a soap solution, water and alcohol, after which it is dried.

In order to free the grains also on the other surface the foil is etched for a few minutes with a 5 percent alcoholic KOH-solution. It is subsequently washed with alcohol and deionized water. After drying the foil is cured at 150° C. for 1 1/4 hours.

A piece of the resultant foil 1, as is shown schematically in FIG. 1 of the drawing, is clamped between two metal masks 2 and 3 of 80 x 32 mm, provided with 40 circular openings of a diameter of 5 mm.

The assembly is arranged in a metal bell 4, which is filled subsequent to evacuation, with argon to a pressure of about 0.1 mm Hg.

By means of a voltage between the masks 2,3 and the bell 4 a gas discharge is initiated so that the foil surface portions accessible through the masks are exposed to ion bombardment. With a distance between the masks 2,3 and the bell 4 of 200 mm and with an applied voltage of 700 V the discharge was maintained for 15 minutes.

After the foil 1, slightly heated by the ion bombardment, is cooled and after evacuation of the bell 4, aluminum is applied from the vapor phase by means of the heating helices 5 and 6 to a layer thickness of about 1 μ .

After the foil is divided in separate portions, products are

obtained which consist, as is shown partly in a sectional view in FIG. 2, of an insulating foil 10 and grains 11 of gallium phosphide embedded therein, which foil is provided on both sides with aluminum layers 12 and 13.

These resistors, formed by a foil portion of 8x8 mm and having circular contact layers of a diameter of 3 mm on both sides, are subjected to a current pulse of 200 mA (about 1 second) between the contact layers.

The resultant resistors have the characteristic curve shown in FIG. 3. It is found that the non-linearity is very high in the voltage range between 3 and 5V, the noise is low and in operation they exhibit substantially no fluctuation.

Moreover, the reproducibility is very good. With a load of 10 mA the voltage measured on ten resistors was found to lie between 4.31 and 4.55 V.

It should be stated that the described results may be obtained with a simple manufacturing process which does not employ either ion bombardment or "forming." However, the best results from a stand point of uniformity and reproducibility are obtained when the processing steps include the ion bombardment and "forming" steps. The particular details of such steps are not critical and other ion bombardment processes and other forming treatments have been successfully employed.

It should be understood that the present invention is not restricted to the given examples and that many variations may be carried out within the scope of the invention. In particular semiconductors having an energy gap of more than 1.12 V other than gallium phosphide may be used, and the foil may comprise a binder material other than polyurethane.

What is claimed is:

1. A voltage-dependent resistor consisting of a foil of electrically insulating material having embedded therein grains of semiconductive material said grains protruding from both surfaces of said foil, having a size of not more than 150 μ and consisting of a semiconductor III-V compound with an energy gap of more than 1.1 eV and metal contact layers electrically interconnecting the protruding grains at least one of said contact layers forming metal-semiconductive barriers with said grains.

2. A resistor as claimed in claim 1, characterized in that the semiconductor grains consist of gallium phosphide.

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