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(54) **Protection device.**

(57) A threshold switching device for protecting an electrical circuit from an overvoltage comprises a switching element formed from a chalcogenide glass and a pair of electrodes that are in contact with the composition. When the circuit experiences an overvoltage transient, the switching element will switch to its low resistance state to pass the electrical current to ground and then revert to its high resistance state.

The switching element includes an indium layer or an indium containing layer between the switching element and at least one, preferably both electrodes. The presence of the indium layers improves the adhesion of the electrodes and/or reduces the electrical contact resistance between the chalcogenide glass and the electrodes and thereby increases the amount of electrical energy that may be passed through the device during a voltage transient before the device latches in its low resistance state.

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CIRCUIT PROTECTION DEVICE

This invention relates to circuit protection devices, and especially to devices for protecting electrical circuits against voltage transients that are caused by an electromagnetic pulse, e.g. lightning, and also the transients that are caused by electrostatic discharge.

One class of material that has been proposed for use in the manufacture of circuit protection devices in general are the chalcogenide glasses, by which is meant glasses formed from elements of group VIB of the periodic table (IUPAC l965 revision) together with other elements, especially those of groups IVB and VB, for example as described in U.S. Patent No. 3,27l,59l to Ovshinsky. Certain of these glasses can be used to form "threshold" devices by which is meant devices that will change from a high resistance state to a low resistance state on application of a high voltage (the lowest such voltage being referred to as the "threshold voltage") but which will remain in their low resistance state only for as long as a small "holding" current is maintained. Other chalcogenide glasses can be used to form "memory" devices which will change from a high resistance state to a low resistance state on application of a high voltage and which will remain in the low resistance state, even when no voltage is applied, until an appropriate, different, voltage pulse is applied. As will be appreciated, only threshold devices are appropriate for the production of circuit protection devices.

The chalcogenide glass materials have the advantage that they exhibit very short switching times between their high and low resistance states where the voltage transient that causes switching is significantly higher (e.g. about 50 V or more) than the threshold voltage, typically less than l nanosecond, which is sufficiently fast for protecting circuits from the transient.

In our copending British Application No. 8508304, the entire disclosure of which is incorporated herein by reference, circuit protection devices that are formed from a number of specific germanium/selenium/ arsenic amorphous compositions are described. The devices described therein display surprisingly high "energies to latch", that is to say, the devices can withstand surprisingly high electrical energies due to the voltage transients before they latch permanently in their low resistance state.

Without being bound by any particular theory, it is believed that one factor in determining the quality of the switch is the contact resistance between the chalcogenide glass material and the electrodes, and that a reduction in the contact resistance can increase the energy to latch of the switch even to the extent that the improvement in the energy to latch caused by a substantial reduction in electrode contact resistance may even effectively cause a composition to change from one that exhibits memory characteristics to one that exhibits threshold characteristics. It is accordingly conjectured that the memory characteristics previously observed by Pinto and Ovshinsky et al could, in fact, be caused by a high electrode contact resistance.

According to the present invention, there is provided a threshold switching device which comprises a switching element formed from an amorphous chalcogenide composition and a pair of electrodes that are in contact with the composition, the device containing an indium or indium containing layer in contact with the composition.

By the use of an indium containing layer it is possible in many instances to reduce the electrical contact resistance and thereby to increase the energy to latch of the device to allow optimisation of other properties of the compositions. Preferably the device exhibits an energy to latch of at least 40mJ, more preferably at least 60mJ and especially at least l00mJ for reasons given in our copending European application No. 0l9689l.

Preferably the electrode contact resistance is sufficiently low that the overall electrode-to-electrode resistance of the device (in its low resistance state) is not more than l0 ohms and especially not more than l ohm, the most preferred resistance being less than 0.l ohm.

Another advantage of the use of indium or indium containing interlayers is that the adhesion of the electrode to the switching element can be considerably improved, to the extent that it is possible reliably to form electrical connections to the electrodes by wire bonding techniques. Previously proposed devices have failed on a number of occasions by separation of the electrode from the chalcogenide glass, even after very small electrical transients were applied. The separation, which was often associated with sparking from the electrode, and ultimately complete destruction of the device, can be eliminated or considerably reduced by the use of an interlayer according to the invention.

The present invention is applicable to chalcogenide glass compositions in general, and especially oxygen-free glasses, especially those containing sulphur and/or selenium optionally and preferably together with group IVB and group VB elements such as germanium, silicon, phosphorous, arsenic and antimony. Preferred glasses are those containing germanium, selenium and arsenic, for example those disclosed in our copending British Application described above which contain at least 15 atomic % selenium but preferably not more than 75 atomic % selenium. The arsenic content is preferably at least 10 atomic % but preferably not more than 65 atomic %. In addition or alternatively, the composition preferably contains at least 5 atomic % germanium but not more than 42 atomic % germanium.

The most preferred compositions contain not more than 35 atomic % germanium, more preferably not more than 30 atomic % germanium and especially not more than 25 atomic % germanium. Also, the compositions preferably contain at least 20 atomic % selenium and especially at least 30 atomic % selenium but preferably not more than 70 atomic % selenium and especially not more than 60 atomic % selenium. The compositions preferably contain at least 20 atomic % arsenic and especially at least 25 atomic % arsenic, but preferably not more than 60 atomic % arsenic and especially not more than 55 atomic % arsenic.

It is possible for quantities e.g. up to 10% or sometimes more, of other materials to be present in the compositions used in the devices according to the invention, for example minor amounts of the elements antimony, bismuth, silicon, tin, lead, halogens and some transition metals provided that the presence of such materials does not deleteriously affect the properties, such as the energy to latch and/or off resistivity, to a significant degree. It is preferred, however, for the compositions to contain substantially no tellurium since the presence of tellurium has been found to reduce the off resistivity of the materials severely, although, in certain circumstances, small quantities of tellurium may be tolerated, e.g. up to 10 atomic %, but preferably less than 5 atomic %.

The films of glass and metals are preferably deposited by vacuum techniques such as vacuum evaporation or d.c. (in the case of metals) or r.f. (in the case of chalcogenide glass) maagnetron sputtering. The vapour may be generated by heating an appropriate mixture of the components (not necessarily having the same composition as the intended glass) or the separate components may simultaneously be heated.

In one preferred method of forming the device, a substrate of suitable electrode design and masked to the desired pattern is coated sequentially with indium (to a thickness of about 0.1 to 0.5 micrometre) and then with chalcogenide glass to about 10 micrometres thickness in a vacuum chamber at 10^{-3} to 10^{-4} Pa pressure by evaporating the coating materials from separate resistance heated boats. A second indium interlayer and a top electrode are deposited onto the glass by a similar process, although in order to deposit a thick metal electrode film in a reasonable time, a higher evaporation rate may be achieved by using an electron beam heated source rather than a resistance heated boat. In order to achieve good adhesion and a low contact resistance, the layers should be deposited without releasing the vacuum except where necessary to change or realign masks and then only when the substrates are cold and by admitting an inert gas such as nitrogen or argon, in order to reduce the possibility of surface oxidation or contamination.

In another method, an indium containing chalcogenide glass interlayer of 0.1 to 0.5 micrometres in thickness is formed between the chalcogenide glass switching element and the electrodes by a vacuum evaporation process. Preferably the indium containing glass has the same composition (except for the presence of indium) as that of the switching element, and preferably has an indium content of at least 1%, preferably at least 5% but preferably not more than 30%, more preferably not more than 20% and especially not more than 15% indium, based on the total weight of the glass (including indium).

In a modification of this method an indium layer (e.g. 0.1 micrometre thick) may be provided on each electrode and an indium containing glass interlayer (e.g. about 0.5 micrometre thick) may be provided between the glass forming the switching element and the indium layer. As will be appreciated, this modification is one example of a method of forming a device in which there is a concentration gradient of indium as one penetrates the glass, which varies from about 100% indium adjacent to the electrode to about 0% indium at a depth of 0.3 to 1 micrometre into the glass. This may be achieved in the most preferred method in a variety of ways: for example a number of glass composition having different indium contents ranging from pure indium down to low (e.g. 0.5% indium) may be deposited sequentially onto the electrode and, after deposition of the switching material, may be deposited in reverse order. Alternatively, indium and the switching element glass composition may be deposited from different boats simultaneously at the beginning and end of the deposition process. In this case the electrical power provided to heat the two boats is continuously varied so that a high rate of deposition of indium and a low rate of deposition of glass is achieved adjacent to the electrodes, the deposition rate of indium falling and the glass deposition rate rising as the distance from the electrodes increases.

It is possible for the entire switching element to contain indium. However, in this case the device must include a layer between the switching element and at least one of the electrodes that contains a substantially higher (e.g. at least l0%, especially at least 20 atomic % higher) indium content. In some cases the indium may evaporate at a faster rate than the other components and so the element may have a higher indium content adjacent to one of the electrodes, in which case it may be appropriate to deposit a layer of indium on top of the deposited glass immediately before depositing the second electrode since that part of the glass layer will be depleted in indium.

The dimensions of the switching element used in the device according to the invention will depend on the particular chalcogenide glass composition that is used to form it, although the thickness of the switching element will usually be not more than 40 micrometres, preferably not more than 20 micrometres, but usually at least 5 and preferably at least l0 micrometres. The cross-sectional area of the switching element, in a plane normal to the direction of current flow therethrough, will depend on the maximum current flow. It is preferably at least $0.5mm^2$, the preferred size being about lmm^2 for discrete devices and for the maximum pulse level, at least $2mm^2$.

The devices may be incorporated in an electrical circuit in any suitable position, normally being connected between a current carrying line and earth, (the term "earth" in this context including any structure having an appropriate shape and/or capacity so that it can absorb the charge generated by the transient, and includes for example connection to the chassis and the like in vehicles such as aircraft), and, of course, more than one such device may be employed in the electrical circuit. The devices are conveniently incorporated in other electrical components for example electrical connectors, in which case the device will usually be connected between a current carrying element of the device and a terminal or other part of the device to be earthed e.g. a conductive housing.

Although in most instances the device will revert to its high resistance state as soon as the transient voltage has subsided, it is still possible for the device to be forced into a permanent low resistance state, for example if the current associated with the transient is unduly large or if a number of rapid transients are experienced. As mentioned above, whether or not the device will become permanently conductive depends on the amount of energy absorbed by the device from the transient. In some applications it may be desirable for the protection device to fail in this way, that is to say, so that the equipment is still protected against transients but will not function until the protection device is replaced or reset. In other applications it may be desirable for the device to fail in a high resistance (open circuit) state so that the equipment will carry on functioning although unprotected from subsequent transients. Thus in some cases the device may be connected in series to means that will exhibit a high resistance to the intended electrical circuit current at least when the switching element has become permanently conductive. Thus, for example, the switching element may be connected to the current carrying line or to earth via a fuse or switch that is capable of transmitting currents passed through it when the switching element is in its threshold mode but will change to a high resistance state when the switching device has become permanently conductive.

Alternatively or in addition, the device may include a capacitor to ensure that the device exhibits a high resistance to all frequencies below the cut-off limit of the capacitor. The use of a capacitor in series with the switching element has a number of advantages as mentioned in our copending British Patent Application No. 8508305 entitled "Overvoltage protection Device: filed on 29th March, l985, the disclosure of which is incorporated herein by reference. Briefly, the use of a capacitor of appropriate size, for example from l0pF to 2 microfarads in series with the switching element will enable the transient current to be transmitted to earth, since most of the power of the transient current occurs at frequencies above l0 kHz, but will exhibit a high impedance to the intended currents in the circuit which will have significantly lower frequencies or will be a direct current. Also, the use of a capacitor will prevent or significantly reduce the possibility of the switching element latching in its low resistance state after a transient has occurred. Such latching may occur in the absence of a capacitor due to direct current flow through the switching element keeping the switching element in its low resistance state.

A device in accordance with the present invention and articles that incorporate the device will now be described by way of example with reference to the accompanying drawings, in which:

Figure l is a sectional view of a device in accordance with the invention with the thickness grossly exaggerated for the sake of clarity;

Figure 2 is a side view, partly in section, of a BNC coaxial connector that incorporates a circuit pro tection device according to the invention;

Figure 3 is a side view, partly in section, of a flat cable mass termination connector and wafers that incorporate a circuit protection device according to the invention;

Figure 4 is an enlarged view of part of the connector shown in figure 3; and

Figure 5 is a perspective view of a modification of the wafers shown in figure 3;

Figure I of the drawings shows schematically a circuit protection device in accordance with the present invention. The device has been formed by depositing 0.I micrometre thick indium layer 20I onto a copper electrode 202 by a vacuum evaporation method, followed by a I0 micrometre thick germanium/arsenic/selenium glass layer 2I0, a further indium layer 203 and a further copper electrode 204, the further layers all being formed by vacuum evaporation from resistance heated boats with the exception of the copper electrode 204 which was formed by electron-beam evaporation. Adjacent to the indium layers 20I,203 are two further layers 205,206 which comprise the germanium/arsenic/selenium glass and a small quantity of indium. The layers 205,206 may be formed by diffusion of part of the indium from layers 20I,203 into the glass layer 202 or may be formed as a separate layer by any of the methods described above.

Referring to figure 2 of the accompanying drawings, a connection arrangement for connecting two coaxial cables comprises a connector shell I and a male connector 2. The male connector 2 comprises a pin 3, the central and rear portion of which is hollow for receiving the central conductor of a coaxial cable to be connected (not shown). The pin has a fluxed solder ring 4 and a number of apertures (not shown) beneath the solder ring which communicate between the solder ring 4 and the hollow interior of the pin 3. The rear end I0 of the pin is firmly located in a connector housing 5 by means of an electrically insulating plastics spacer 6. The housing 5, which provides the electrical connection between the shields of the cables to be connected, has a termination portion 7 on which is mounted a solder impregnated braid 8 and solder ring 9.

The rear end I0 of the pin is provided on its outer surface with an electrode, e.g. a copper electrode followed by a I0 micrometre thick switch element having an indium/chalcogenide glass/indium construction that has been formed thereon by a vapour deposition method, and the outer surface of the glass element II has been provided with a further thin (about I0 micrometres thick) electrode, e.g. formed from copper by an electron beam evaporation method. The electrode is electrically connected to the housing 5 by means of a column or wire I2 of solder or other suitable conductive material.

In order to connect a coaxial cable to the connector, the outer jacket, shield and dielectric are cut back by appropriate amounts and the cable inserted into the connector so that the exposed end of the internal conductor is located within the hollow interior of the pin 3, the dielectric abuts the rear end of the spacer 6 and the exposed shield is located within the solder impregnated braid 8. The connector is then briefly heated, for example by means of a hot-air gun, to fuse the solder rings 4 and 9 and to form solder connections between the pin 3 and central conductor and between the braid 8 and coax cable shield.

The connector will function exactly as a standard coaxial connector until the connected cable experiences a voltage transient whereupon the potential difference across the thickness of the glass layer II will cause the glass to become electrically conductive and form a closed circuit between the central conductor and the shield.

Referring to figures 3 and 4, a mass termination connector such as that described in British Patent No. I,522,485 (the disclosure of which is incorporated herein by reference) is schematically shown.

The connector comprises a connector housing 2I and a pair of connector wafers 22 and 23 that can be inserted into the housing. Each wafer 22,23 has a number of (usually 20 or 40) metallic electrical conductors 24 extending therethrough which terminate at one end either in the form of pins 25 or complementary "tuning fork" female contacts and at the other end in the form of contacts 26 for connection to a flat cable or to a number of small single conductor wires. The particular means used for connecting the conductors 24 to the wires or flat cable is not shown but usually comprises one or more solder devices for example as described in U.S. Patent Specification No. 3,852,5I7.

In each of the wafers 22 and 23 a stepped recess 27 is made that extends across the width of the entire wafer to expose each of the conductors. in one embodiment of this connector, a copper electrode is deposited onto the individual conductors 24 followed by a 0.I micrometre thick indium layer, a I0 micrometre thick layer 28 of the selenium-germanium-arsenic glass described above, a further 0.I micrometre thick indium layer and a thin, e.g. about I0 micrometres thick, electrode 29 formed e.g. from copper, gold or aluminium on top of the indium layer. An additional conductive layer 30 or "ground plane" of gold or aluminium is located on the wafer material in the stepped recess 27, the ground plane being electrically earthed for example to the metallic housing of the connector or to an earth pin. Each electrode 29 is connected to the ground plane by means of a wire 3I formed from e.g. gold or aluminium and bonded to the electrode 29 and ground plane 30 by conventional wire bonding techniques.

Alternatively, a single layer 28 of the glass, indium and electrode 29 may be deposited across the entire width of the wafer (except for a single conductor which is to act as the ground conductor) in which case only a single wire 3I is necessary for connection to the ground plane. Alternatively the ground plane and wire can even be dispensed with if the chalcogenide glass layer 28, and indium and electrode 29 are deposited over all the conductors 24.

In an alternative construction, the selenium-germanium-arsenic glass layer, indium layersand electrodes are deposited onto the common ground plane 30, and the wires 3l connect the conductors 24, after any appropriate surface preparation if necessary, with the electrode of the glass layer.

Figure 5 shows schematically a further modification of the wafer shown in figures 3 and 4. In this form of wafer the glass layers 28, indium layers and electrodes 29 are deposited on the conductors 24 as described above and are electrically connected to a ground plane 30 by means of wires 3l. In addition, however, a l00 nano-farad capacitor 40 is located in the recess 27 and is connected between the ground plane and an earth terminal or housing of the connector. In this form of device any transient current having a frequency spectrum above about l MHz is conducted directly to earth while any direct currents or alternating currents of frequencies significantly lower than about l MHz are blocked by the capacitor. This modification of the device has the advantage that it reduces or eliminates the possibility of the glass switching layers 28 being held in their low resistance state by the direct currents in the electrical system after the transient has been transmitted to earth.

Examples l to 3

A $Ge_{14}\,As_{34}\,Se_{52}$ glass was formed by mixing the components, which were of at least 99.99% purity, and melting the mixture in a silica ampoule under a vacuum or under reduced argon pressure. During melting, which was carried out at temperatures of up to l000°C and for periods of up to 48 hours, the ampoule was rocked to ensure that a homogeneous melt was obtained.

A l0 micometre thick layer of the glass so prepared was formed by vapour deposition at a pressure of 10^{-3} to 10^{-4} Pa using a resistance heated source. Deposition rates of 0.3 to l.0 micrometres per minute were employed. The layer was provided with a number of electrodes of varying electrode contact resistance, and the energy to latch of the switch devices so formed was determined as described above.

In Example l a gold spring probe of l mm diameter was applied to the top surface of the glass layer with a force of lg.wt., the opposite surface being provided with a copper film electrode.

In Example 2 copper electrode was provided on each surface of the glass layer by a vacuum evaporation method. However the electrodes were allowed partially to oxidize by readmission of air into the vacuum chamber while the electrodes were hot.

In Example 3 a 0.5 micrometre thick layer of the same glass composition but containing l5% indium was provided on each surface of the glass layer and 0.l micrometre thick layer of indium was provided between each indium containing glass and (unoxidized) vacuum deposited copper electrodes. The results are shown in table l.

In Example 4 a 0.2 micrometre thick layer of indium was provided between the chalcogenide glass and each electrode by vacuum evaporation from a resistance heated boat. In Example 5 the same procedure as Example 4 was used with the exception that the indium layers each had a thickness of 0.05 micrometres.

TABLE I

Example	Threshold Voltage(V)	Energy to Latch (mJ)	Voltage across Electrodes (in low resistance state)(V)
1(comp.)	80	<5	20
2(comp.)	110	25	20
3	110	200	<2
4	100	160	2
5	110	130	5

The energy to latch of the device, and hence of the glass material, was measured by means of a circuit as shown in figure 6. Single shot pulses generated by means of a pulser I were passed to the switching element 2 connected in series with a current limiting resistor 3 having a resistance R_2 of from 40 to I00 ohms and the voltage across the switching element was observed by means of oscilloscope 4. The voltage generated by the pulser I was gradually increased (about 5 to I0 pulses being passed for each voltage level from the pulser) until the switching element latched in its low resistance state (determined by subsequently measuring its resistance.

The energy to latch the device, E_L was determined by the equation:

$$E_L = J.\frac{V^2}{(1000)}.\frac{R_1}{(R_1+R_2)}$$

where J is the energy available from the pulser;
V is the peak voltage from the pulser when latching occurred;
R_1 is the internal output impedance of the pulser (5 ohms); and
R_2 is the resistance of the current limiting resistor.

This equation gives very good agreement with values obtained by integrating the current and voltage curves of the pulses.

The resistance across the device was determined by replacing the device with standard resistances and comparing the voltage/time curve with that of the device when subjected to standard pulses. It was observed that the peak current flowing through the device was approximately I ampere in all cases so that the resistance across the device (in ohms) is numerically equal to the voltage across the electrodes (in volts).

Claims

I. A threshold switching device which comprises a switching element formed from an amorphous chalcogenide composition and a pair of electrodes that are in contact with the composition, the device containing an indium or indium containing layer between the composition and at least one of the electrodes.

2. A device as claimed in claim I, which has an electrode-to-electrode resistance, in its low resistance state, of not more than I0 ohms.

3. A device as claimed in claim 2, which has an electrode-to-electrode resistance, in its low resistance state, of not more than I ohm.

4. A device as claimed in claim 3, which has an electrode-to-electrode resistance, in its low resistance state, of not more than 0.I ohm.

5. A device as claimed in any one of claims I to 4, wherein the chalcogenide glass composition comprises germanium, selenium and arsenic.

6. A device as claimed in any one of claims I to 5, wherein the concentration of indium in the or each indium containing layer increases toward the or each electrode.

7. A device as claimed in any one of claims I to 6, wherein the or at least one indium or indium containing layer comprises an indium containing chalcogenide layer in contact with the switching element, and a layer substantially completely consisting of indium between the indium containing chalcogenide layer and the electrode.

8. An electrical component which includes a threshold switching device as claimed in any one of claims I to 7 between a current carrying line of the circuit and earth.

9. A component as claimed in claim 8, which is an electrical connector.

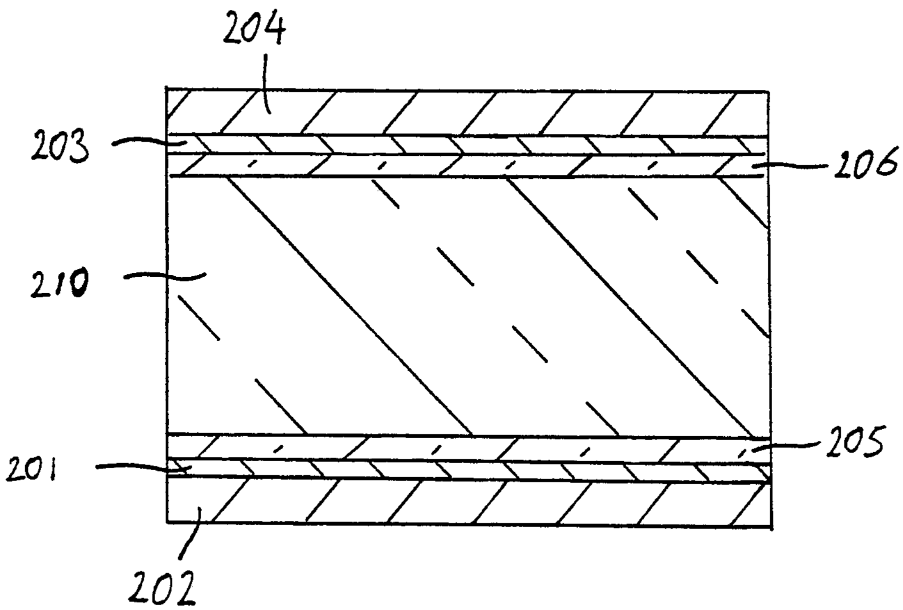


FIG. 1

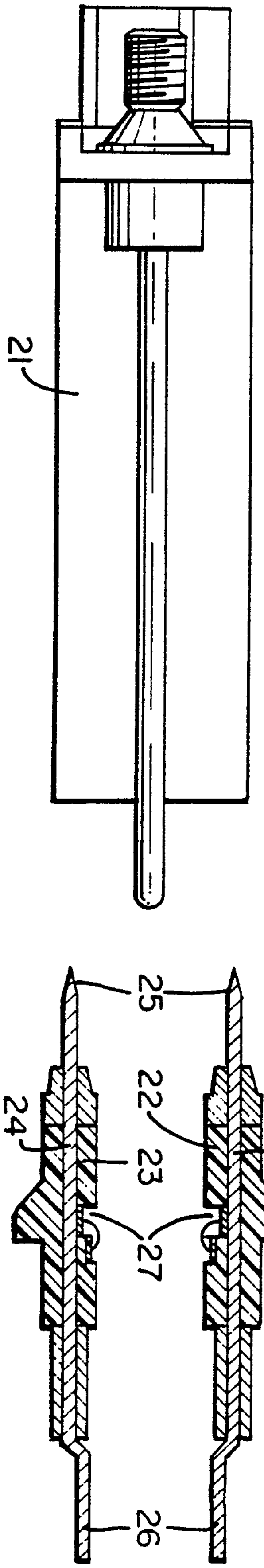


Fig. 3

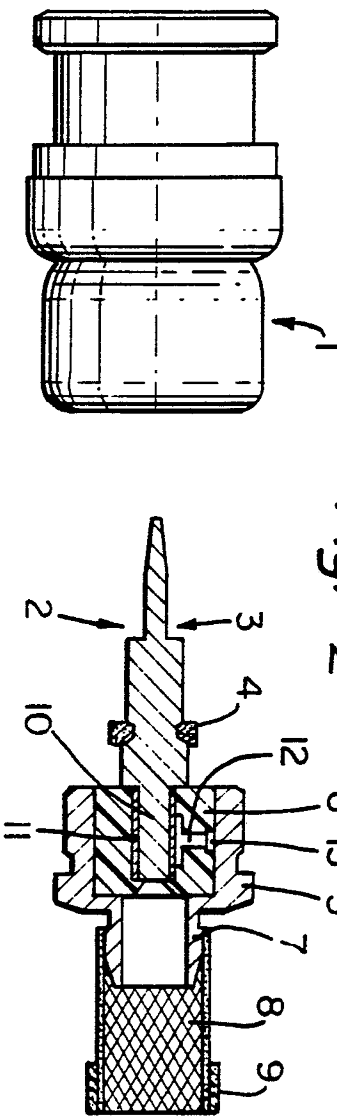


Fig. 2

Fig. 4

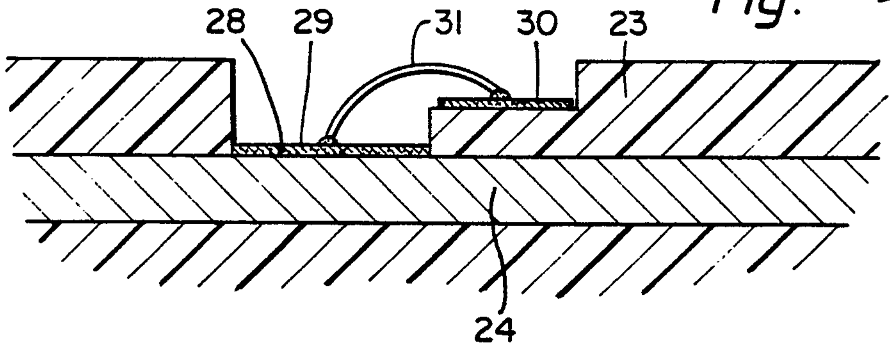
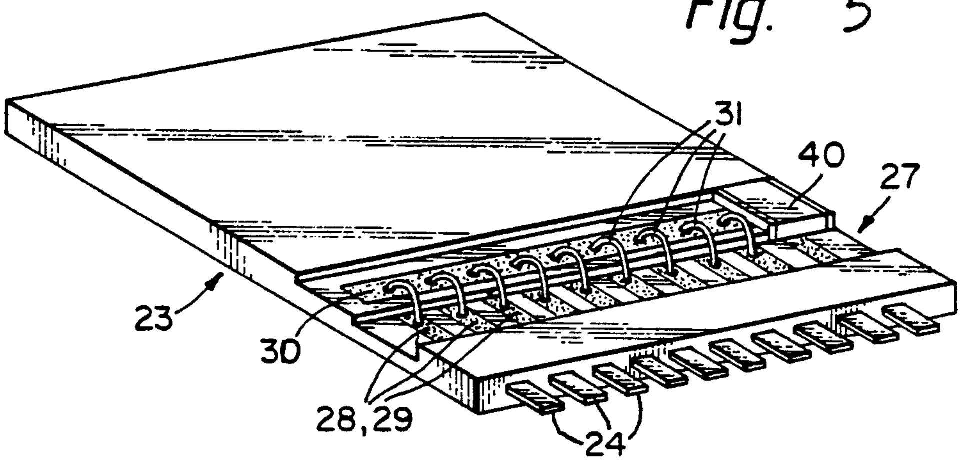


Fig. 5



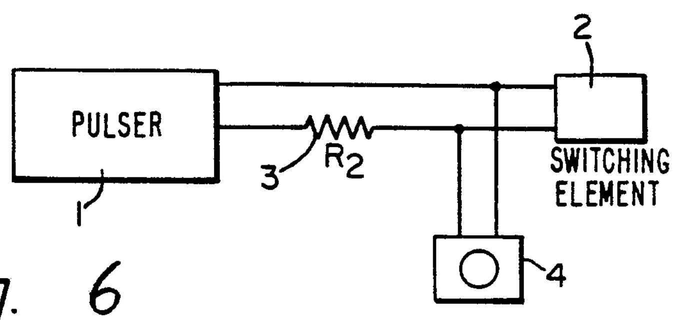


Fig. 6