

[54] **METHOD OF MAKING A CURRENT CONTROLLING DEVICE INCLUDING VO₂**

[75] Inventors: **Gordon R. Fleming**, Pontiac;
Stanford R. Ovshinsky, Bloomfield Hills, both of Mich.

[73] Assignee: **Energy Conversion Devices, Inc.**,
Troy, Mich.

[22] Filed: **Sept. 8, 1970**

[21] Appl. No.: **70,155**

Related U.S. Application Data

[60] Division of Ser. No. 830,581, May 27, 1969, Pat. No. 3,588,638, which is a continuation-in-part of Ser. No. 809,580, March 24, 1969, abandoned.

[52] **U.S. Cl.** **264/104**; 264/109; 264/123;
427/82; 427/215; 427/343; 427/377

[51] **Int. Cl.** **C04b 35/00**; B29g 7/00

[58] **Field of Search** 117/200, 201, 221, 100 B,
117/62; 252/518; 264/109, 123, 104

[56] **References Cited**

UNITED STATES PATENTS

3,402,131	9/1968	Futaki et al.	252/518 X
3,484,611	12/1969	Futaki	252/518 X
3,503,902	3/1970	Shimoda	252/518 X
3,557,026	1/1971	Teeg et al.	252/518
3,562,188	2/1971	Mitsuishi et al.	252/518

FOREIGN PATENTS OR APPLICATIONS

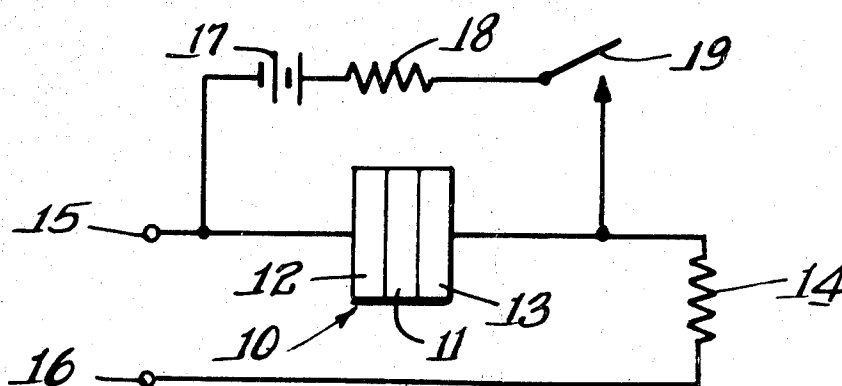
184,714	9/1936	Switzerland	252/518
---------	--------	-------------	---------

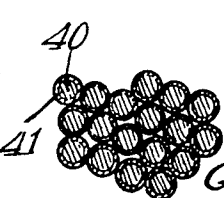
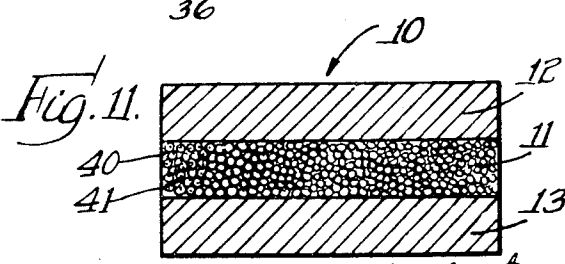
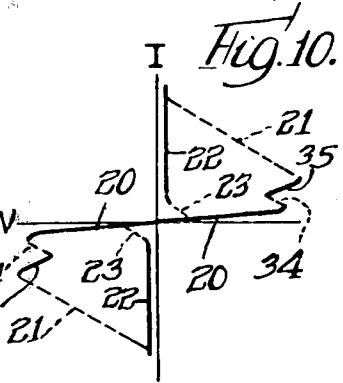
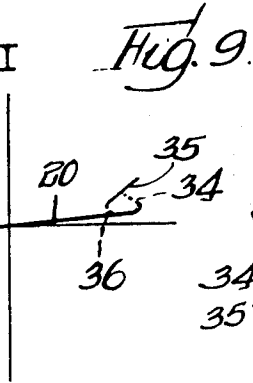
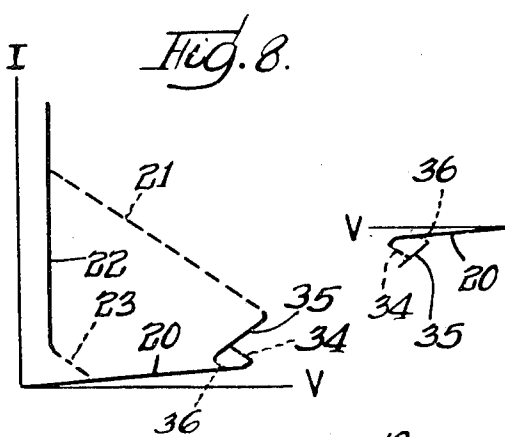
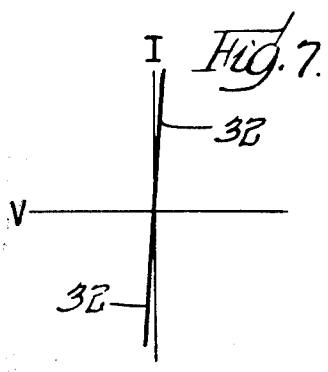
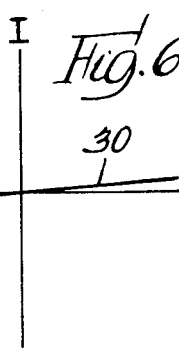
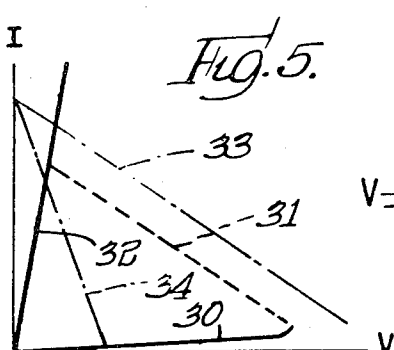
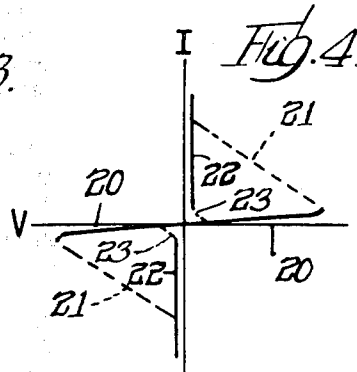
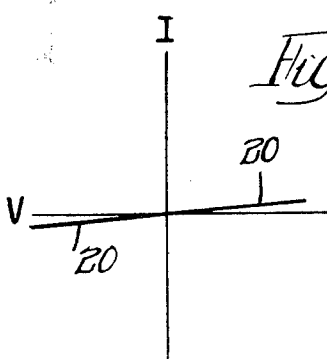
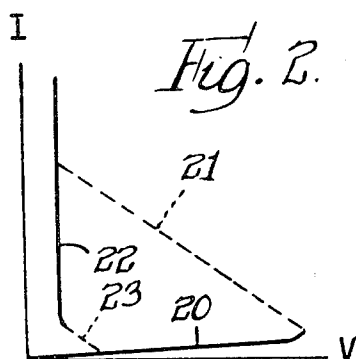
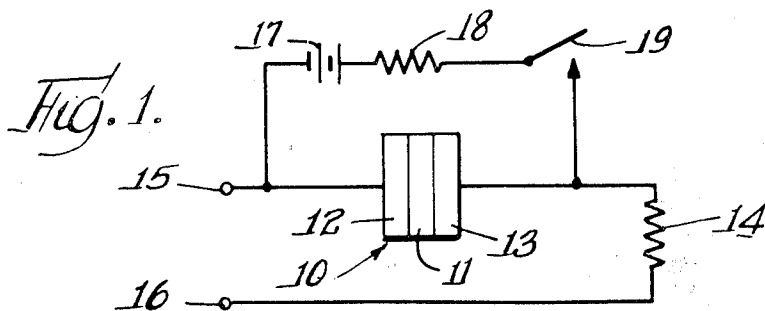
Primary Examiner—Michael F. Esposito

[57] **ABSTRACT**

A current controlling device for an electrical circuit including a semiconductor element and electrodes in low electrical resistance contact therewith, wherein said semiconductor element has a threshold voltage value and a high electrical resistance to provide a blocking condition for substantially blocking current therethrough, wherein the high electrical resistance is substantially instantaneously decreased to a low resistance in response to a voltage above said threshold voltage value to provide a conducting condition for substantially conducting current therethrough, wherein the semiconductor element comprises high electrical resistance refractory powder particles substantially individually coated with a thin solid coating of substantially VO₂, wherein the high electrical resistance refractory powder particles may comprise SnO₂, SiO₂, Al₂O₃, ZrO₂ or TiO₂ or the like, wherein the thin substantially VO₂ coating on the particles is obtained from V₂O₅ and/or V₂O₃ in the formation thereof by several methods described herein, wherein the devices may be of the non-memory type or the memory type, and wherein the devices may have an intermediate or partial conducting condition.

11 Claims, 12 Drawing Figures





Inventors
Gordon R. Fleming
Stanford R. Ovshinsky
By: Wallenstein, Spangenberg, Hatten & Strampel Attys

METHOD OF MAKING A CURRENT CONTROLLING DEVICE INCLUDING VO₂

This application is a division of Gordon R. Fleming and Stanford R. Ovshinsky application Ser. No. 830,581, filed May 27, 1969, now U.S. Pat. No. 3,588,638 which in turn is a continuation-in-part of Gordon R. Fleming and Stanford R. Ovshinsky application Ser. No. 809,580, filed Mar. 24, 1969 (now abandoned).

The invention of this application is related to and is an improvement upon the invention disclosed in Stanford R. Ovshinsky U.S. Pat. No. 3,271,591 issued Sept. 6, 1966. That patent discloses two basic types of current controlling devices, a non-memory type device (referred to therein as a "Mechanism" device) and a memory type device (referred to therein as "Hi-Lo" and "Circuit Breaker" devices). Both the non-memory and memory type devices are changed from their blocking condition to their conducting condition by applying a voltage above a voltage threshold value. The non-memory type device requires a holding current to maintain it in its conducting condition and it immediately returns to its blocking condition when the current decreases below a minimum current holding value. The memory type device requires no holding current, it remaining in its conducting condition even though the current is removed or reversed, and it is returned to its blocking condition by a current pulse of at least a threshold current value. The invention herein is applicable to both types of current controlling devices.

A principal object of this invention is to provide an improved current controlling device for accomplishing the current controlling or switching functions substantially as performed by the current controlling devices of the aforementioned U.S. Pat. No. 3,271,591. Another object of this invention is to provide a current controlling device having an intermediate or partial conducting condition.

Another principal object of this invention is to provide improved methods for making the semiconductor elements of the current controlling devices.

The current controlling devices of this invention, while utilizing substantially VO₂ in the semiconductor element thereof, are considerably different in construction, manner of operation and results obtained from the Neel effect switching devices of Handelman U.S. Pat. No. 3,149,298 wherein the devices of said patent utilize pure single crystals of various described vanadium-oxygen compounds, which are thermally biased close to selected temperatures for the various selected crystals, which are thermally cycled above and below said selected temperatures for switching purposes, and which have relatively small conductivity differences between their switched conditions.

Briefly, the semiconductor elements of the current controlling devices of this invention which are contacted by the electrodes comprise high electrical resistance refractory powder particles which are substantially individually coated with a thin solid coating of substantially VO₂. Such refractory powder particles preferably comprise SnO₂, SiO₂, Al₂O₃, ZrO₂ or TiO₂ or the like. The thin solid coating of substantially VO₂ may be substantially polycrystalline and may contain minor amounts of the SnO₂, SiO₂, Al₂O₃, ZrO₂ or TiO₂ therein. These coated particles may be formed into the semiconductor element in various ways, as for example, compacting them into pellets, or incorporating

them in substantially contacting engagement in a carrier such as paint or glass or the like.

Because of the thin coating of the substantially VO₂ on the high electrical resistance refractory powder particles, the semiconductor element has a high electrical resistance in its blocking condition which is much higher than where crystalline VO₂ itself would be interposed between the electrodes. In this respect, the coated partialized structure forms elongated tortuous paths through the coatings about the particles between the electrodes which are of high resistance. In the inhomogeneous polycrystalline coated particles there are no special requirements for purity and stoichiometry as would be required in single crystals. The current controlling devices of this invention operate at room temperature and no thermal biasing is necessary. There is no problem with structural degeneration as is experienced in cycling single crystals. Resistivity changes between the blocking condition and the conducting condition are much larger than those in single crystals. Field induced electronic excitation without concomitant temperature increase sufficient to reach a transition point is also possible to obtain switching of the devices of this invention.

The substantially VO₂ thinly coated refractory powder particles may be formed in various ways. For example, V₂O₅ powder particles may be mixed with the refractory powder particles within a molar percent range of about 5 to 25% of VO₂ and heated in a reducing atmosphere to a temperature between the melting point of V₂O₅ and the melting point of VO₂ to melt the V₂O₅ powder particles and form substantially VO₂ and individually coat the refractory powder particles with the thin solid coating of substantially VO₂. As another example, V₂O₅ powder particles and V₂O₃ powder particles in substantially equal molar percent are mixed with the refractory powder particles within a molar percent range of about 5% to 25% of said V₂O₅ and V₂O₃ and heated in a substantially inert atmosphere to a temperature between the melting points of V₂O₅ and V₂O₃ and the melting point of VO₂ to melt the V₂O₅ and V₂O₃ powder particles and form substantially VO₂ and individually coat the refractory powder particles with the thin solid coating of substantially VO₂. By utilizing the aforementioned mole percent range of 5 to 25% the individual coating of the refractory powder particles with the thin coating of substantially VO₂ is assured so that the resultant product is still substantially in powder or partialized form rather than in a mass form which would require subsequent crushing and, hence, a less uniform product.

As a further example, a V₂O₅ sol having charged V₂O₅ particles colloiddally suspended therein may be formed, and the refractory powder particles may be mixed with said V₂O₅ sol for attracting the charged V₂O₅ particles from said V₂O₅ sol to the surfaces of the refractory powder particles to provide the same with a thin coating of V₂O₅. The mixture may then be dried and heated in a reducing atmosphere to reduce the V₂O₅ to substantially VO₂ and individually coat the refractory powder particles with said thin coating of substantially VO₂. The V₂O₅ sol may be formed by suspending V₂O₅ in water and mixing with H₂O₂ to form a liquid having peroxyvanadates in solution in the water, boiling the solution to decompose the peroxyvanadates back to V₂O₅ to form the V₂O₅ sol having the charged V₂O₅ particles colloiddally suspended therein.

It has been found that by using as the refractory powder particles SnO_2 , SiO_2 , Al_2O_3 or ZrO_2 extremely satisfactory non-memory type current controlling devices are obtained. It has also been found that by using TiO_2 as the refractory powder particles extremely satisfactory memory type current controlling devices are obtained. It has been further found that where ZrO_2 , and sometimes Al_2O_3 , are used as the refractory powder particles double switching actions may be obtained in a non-memory type current controlling device. In this latter respect, the device switches from a blocking condition to a partially conducting condition upon the application of a voltage above a first threshold voltage value, and it switches from the partially conducting condition to a substantially fully conducting condition upon the application of a voltage above a second threshold voltage value. Such a device is extremely useful in computer logic circuits or the like to produce additional points of reference. This device can also be returned from the partially conducting condition and the substantially fully conducting condition directly to the blocking condition when the current through the device decreases below minimum current holding values.

Other objects and advantages of this invention will become apparent to those skilled in the art upon reference to the accompanying specification, claims and drawing in which:

FIG. 1 is a diagrammatic illustration of the current controlling device of this invention connected in series in a load circuit;

FIG. 2 is a voltage current curve illustrating the operation of the non-memory type current controlling device of this invention in a D.C. load circuit;

FIGS. 3 and 4 are voltage current curves illustrating the symmetrical operation of the non-memory type current controlling device and the operation thereof when included in an A.C. load circuit;

FIG. 5 is a voltage current curve illustrating the operation of the memory type current controlling device of this invention in a D.C. load circuit;

FIGS. 6 and 7 are voltage current curves illustrating the symmetrical operation of the memory type current controlling device and the operation thereof when included in an A.C. load circuit;

FIG. 8 is a voltage current curve illustrating the operation of the non-memory type current controlling device of this invention in a D.C. load circuit where the device switches from a blocking condition to a partially conducting condition and from the partially conducting condition to a substantially fully conducting condition;

FIGS. 9 and 10 are voltage current curves illustrating the symmetrical operation of the non-memory type current controlling device illustrated in FIG. 8 and the operation thereof when included in an A.C. load circuit;

FIG. 11 is an enlarged diagrammatic view of the current controlling device showing the VO_2 coated refractory particles arranged between a pair of electrodes; and

FIG. 12 is an enlarged view of the semiconductor material illustrated in FIG. 11 illustrating in more detail the VO_2 coated refractory particles.

Referring first to FIGS. 11 and 12, the current controlling device of this invention is generally designated at 10. It includes a semiconductor material 11 at such as described above arranged between a pair of electrodes 12 and 13. The semiconductor material 11 is of

one conductivity type and is of high electrical resistance and the pair of electrodes 12 and 13 in as 11 contact with the semiconductor material have a low electrical resistance of transition therewith. The high electrical resistance refractory powder particles which may comprise SnO_2 , SiO_2 , Al_2O_3 , ZrO_2 or TiO_2 or the like are designated at 40 and the thin solid coating of substantially VO_2 for these refractory powder particles is designated at 41. The VO_2 coating 41 on these refractory particles 40 may be accomplished in the manner described above. These coated particles 40, 41 may be formed into the semiconductor element in various ways, as for example, compacting them into pellets, or incorporating them into substantially contacting engagement in a carrier such as paint or glass or the like. The electrodes 12 and 13 may be made to contact the semiconductor materials 11 in various ways. They may be mechanically pressed in contact therewith, they may be hot pressed into the semiconductor material, and they may be deposited thereon by vacuum deposition, sputtering, or deposition from a solution or the like. Alternatively, the semiconductor material may be deposited on the electrodes by brushing, silk screening, painting or the like. The electrodes should be good electrical conductors and should not react unfavorably with the semiconductor material. As for example, the electrodes may comprise refractory metals, such as, tungsten, tantalum, molybdenum, columbium or the like, or metals, such as, stainless steel, nickel, chromium or the like. The paint or glass type semiconductor elements have particular utility for use in conjunction with electroluminescent panels wherein the semiconductor elements may be readily applied thereto by painting or silk screening or the like for controlling the same.

Referring now to the diagrammatic illustration of FIG. 1, the current controlling device 10 of this invention having the semiconductor material 11 and the electrodes 12 and 13 is connected in series in an electrical load circuit having a load 14 and a pair of terminals 15 and 16 for applying power thereto. The power supplied may be a D.C. voltage or an A.C. voltage as desired. The circuit arrangement illustrated in FIG. 1, and as so far described, is applicable for the non-memory type of current controlling device. If a memory type of current controlling device is utilized, the circuit also includes a source of current 17, a low resistance 18 and a switch 19 connected to the electrodes 12 and 13 of the current controlling device. The purpose of this auxiliary circuit is to switch the memory type device from its conducting condition to its blocking condition. The resistance value of the resistance 18 is considerably less than the resistance value of the load 14.

FIG. 2 is an I-V curve illustrating the D.C. operation of the non-memory type current controlling device 10 and in this instance the switch 19 always remains open. The device 10 is normally in its high resistance blocking condition and as the D.C. voltage is applied to the terminals 15 and 16 and increased, the voltage current characteristics of the device are illustrated by the curve 20, the electrical resistance of the device being high and substantially blocking the current flow there-through. When the voltage is increased to a threshold voltage value, the high electrical resistance in the semiconductor material substantially instantaneously decreases in at least one path between the electrodes 12

and 13 to a low electrical resistance, the substantially instantaneous switching being indicated by the curve 21. This provides a low electrical resistance or conducting condition for conducting current therethrough. The low electrical resistance is many orders of magnitude less than the high electrical resistance. The conducting condition is illustrated by the curve 22 and it is noted that there is a substantially linear voltage current characteristic and a substantially constant voltage characteristic which are the same for increase and decrease in current. In other words, current is conducted at a substantially constant voltage. In the low resistance current conducting condition the semiconductor element has a voltage drop which is a minor fraction of the voltage drop in the high resistance blocking condition near the threshold voltage value.

As the voltage is decreased, the current decreases along the curve 22 and when the current decreases below a minimum current holding value, the low electrical resistance of said at least one path immediately returns to the high electrical resistance as illustrated by the curve 23 to re-establish the high resistance blocking condition. In other words, a current is required to maintain the non-memory type current controlling device in its conducting condition and when the current falls below a minimum current holding value, the low electrical resistance immediately returns to the high electrical resistance.

The non-memory current controlling device 10 of this invention is symmetrical in its operation, it blocking current substantially equally in each direction and it conducting current substantially equally in each direction, and the switching between the blocking and conducting conditions being extremely rapid. In the case of A.C. operation, the voltage current characteristics for the second half cycle of the A.C. current would be in the opposite quadrant from that illustrated in FIG. 2. The A.C. operation of the device is illustrated in FIGS. 3 and 4. FIG. 3 illustrates the device 10 in its blocking condition where the peak voltage of the A.C. voltage is below the threshold voltage value of the device, the blocking condition being illustrated by the curve 20 in both half cycles. When, however, the peak voltage of the applied A.C. voltage increases above the threshold voltage value of the device, the device is substantially instantaneously switched along the curves 21 to the conducting condition illustrated by the curves 22, the device switching during each half cycle of the applied A.C. voltage. As the applied A.C. voltage nears zero so that the current through the device falls below the minimum current holding value, the device switches along the curve 23 from the low electrical resistance condition to the high electrical resistance condition illustrated by the curve 20, this switching occurring near the end of each half cycle.

For a given configuration of the non-memory device 10, the high electrical resistance may be about 1 megohm and the low electrical resistance about 10 ohms, the threshold voltage value may be about 20 volts and the voltage drop across the device in the conducting condition may be less than 1 volt, and the switching times may be in nanoseconds or less. It has been found that by using as the refractory powder particles SnO_2 , SiO_2 , Al_2O_3 or ZrO_2 extremely satisfactory non-memory type current controlling devices are obtained.

FIG. 5 is an I-V curve illustrating the D.C. operation of the memory type current controlling device 10. The

device is normally in its high resistance condition and as the D.C. voltage is applied to the terminals 15 and 16 and increased, the voltage current characteristics of the device are illustrated by the curve 30, the electrical resistance of the device being high and substantially blocking the current flow therethrough. When the voltage is increased to a threshold voltage value, the high electrical resistance in the semiconductor element 11 substantially instantaneously decreases in at least one path between the electrodes 12 and 13 to a low electrical resistance, the substantially instantaneous switching being indicated by the curve 31. The low electrical resistance is many orders of magnitude less than the high electrical resistance. The conducting condition is illustrated by the curve 32 and it is noted that there is substantially ohmic voltage current characteristic. In other words, current is conducted substantially ohmically as illustrated by the curve 32. In the low resistance current conducting condition the semiconductor material has a voltage drop which is a minor fraction of the voltage drop in the high resistance blocking condition near the threshold voltage value.

As the voltage is decreased, the current decreases along the curve 32 and due to the ohmic relation the current decreases to zero as the voltage decreases to zero. The memory type current controlling device has memory of its conducting condition and will remain in this conducting condition even though the current is decreased to zero or reversed until switched to its blocking condition as hereafter described. The load line of the load circuit is illustrated at 33, it being substantially parallel to the switching curve 31. When a D.C. current pulse is applied independently of the load circuit to the memory type device as by the voltage source 17, low resistance 18 and switch 19 in FIG. 1, the load line for such current is along the line 34 since there is very little, if any, resistance in this control circuit, and as the load line 34 intersects the curve 30, the conducting condition of the device is immediately reentered and switched to its blocking condition. The memory type device will remain in its blocking condition until switched to its conducting condition by the reapplication of a threshold voltage to the device through the terminals 15 and 16.

The memory type current controlling device 10 of this invention is also symmetrical in its operation, it blocking current substantially equally in each direction and it conducting current substantially equally in each direction, and the switching between the blocking and conducting conditions being extremely rapid. In the case of A.C. operation, the voltage current characteristics for the second half cycle of the A.C. current would be in the opposite quadrant from that illustrated in FIG. 5. The A.C. operation of the memory type device is illustrated in FIGS. 6 and 7. FIG. 6 illustrates the device 10 in its blocking condition where the peak voltage of the A.C. voltage is below the threshold voltage value of the device, the blocking condition being illustrated by the curve 30 in both half cycles. Thus, the device blocks current equally in both half cycles. When, however, the peak voltage of the applied A.C. voltage increases above the threshold value of the memory type device, the device substantially instantaneously switches to the conducting condition illustrated by the curve 32 and it remaining in this conducting condition regardless of the reduction of the current to zero or the

reversal of the current. This symmetrical conducting condition is illustrated by the curve 32 in FIG. 7.

When the switch 19 is manipulated to apply a current pulse above a threshold current value and the voltage applied to the terminals 15 and 16 is below the threshold voltage value, the memory type current controlling device is immediately switched to its blocking condition as illustrated by the curve 30 in FIG. 6. For a given configuration of the memory type device, the high electrical resistance may be about 1 megohm and the low electrical resistance about 10 ohms, the threshold voltage value may be about 20 volts and the switching times are extremely rapid. It has been found that by using TiO_2 as the refractory powder particles extremely satisfactory memory type current controlling devices are obtained.

The foregoing operations of the non-memory device and the memory device are like those disclosed in the aforementioned patent and, therefore, a further description thereof is not considered necessary here.

FIG. 8 is an I-V curve illustrating the D.C. operation of the non-memory type current controlling device 10 wherein double switching actions are obtained. The device 10 is normally in its high resistance blocking condition and as the D.C. voltage is applied to the terminals 15 and 16 and is increased, the voltage current characteristics of the device are illustrated by the curve 20, the electrical resistance of the device being high and substantially blocking the current flow therethrough. When the voltage is increased to a first threshold voltage value, the high electrical resistance in the semiconductor material substantially instantaneously decreases in at least one path between the electrodes 12 and 13 to an intermediate electrical resistance value, the substantially instantaneous switching being indicated by the curve 34. This provides an intermediate electrical resistance condition for conducting current therethrough. This intermediate electrical resistance condition is illustrated by the curve 35. As the voltage is decreased, the current decreases along the curve 35 and when the current decreases below a minimum current holding value the intermediate electrical resistance of said at least one path immediately returns to the high electrical resistance as illustrated by the curve 36 to re-establish the high resistance blocking condition. After the device is switched to its intermediate conducting condition as illustrated by the curve 35 as aforesaid and the voltage is increased to a higher threshold voltage value, the intermediate electrical resistance in the semiconductor material substantially decreases in at least one path between the electrodes 12 and 13 to a low electrical resistance, the substantially instantaneous switching being indicated by the curve 21. This provides a low electrical resistance or conducting condition for conducting current therethrough. The low electrical resistance is many orders of magnitude less than the high electrical resistance and the intermediate electrical resistance. This latter conducting condition is illustrated by the curve 22 and it is noted that there is a substantially linear voltage characteristic and a substantially constant voltage characteristic which are the same for increase and decrease in current. In other words, current is conducted at a substantially constant voltage. In the low resistance current conducting condition as indicated by the curve 22, the semiconductor material has a voltage drop which is a

minor fraction of the voltage drop in the high resistance blocking condition near the threshold voltage value.

Here, as in the current controlling device whose voltage and current characteristics are illustrated in FIG. 2, the current decreases along the curve 22 as the voltage is decreased and when the current decreases below a minimum current holding value, the low electrical resistance of said at least one path immediately returns to the high electrical resistance as illustrated by the curve 23 to establish the high resistance blocking condition. In other words, as explained above in connection with the device whose characteristics are illustrated in FIG. 2, a current is required to maintain the current controlling device in its conducting condition and when the current falls below the minimum current holding value, the low electrical resistance immediately returns to the high electrical resistance. Accordingly, the current controlling device whose voltage current characteristics are illustrated in FIG. 8 has substantially three electrical resistance conditions. The high electrical resistance condition illustrated by the curve 20, the intermediate electrical resistance condition illustrated by the curve 35 and the low electrical resistance condition illustrated by the curve 22. The device is switched from the low resistance condition to the intermediate resistance condition by the application of a voltage of a first threshold voltage value and is switched to the low resistance condition by the application of a voltage of a second or higher voltage threshold value. In either instance, when the current through the device is decreased to a minimum current holding value, the device switches from its intermediate electrical resistance condition or its low electrical resistance condition to the high resistance blocking condition.

The current controlling device illustrated in FIG. 8 is symmetrical in its operation, it blocking current substantially equally in each direction and it conducting current substantially equally in each direction, and the switching between the high resistance, intermediate resistance and low resistance conditions being extremely rapid. In the case of A.C. operation, the voltage current characteristics for the second half cycle of the A.C. current would be in the opposite quadrant from that illustrated in FIG. 8. The A.C. operation of this device is illustrated in FIGS. 3, 9 and 10. FIG. 3 illustrates the device in its blocking condition where the peak voltage of the A.C. voltage is below the first threshold voltage value of the device, the blocking condition being illustrated by the curve 20 in both half cycles. When, however, the peak voltage of the applied A.C. voltage increases above the first threshold voltage value of the device, the device is substantially instantaneously switched along the curves 34 to the intermediate electrical resistance condition illustrated by the curves 35, the device switching during each half cycle of the applied A.C. voltage as illustrated in FIG. 9. As the applied A.C. voltage nears zero so that the current through the device falls below the minimum current holding value, the device switches along the curve 36 from the intermediate electrical resistance condition to the high electrical resistance condition illustrated by the curve 20, this switching occurring during the end of each half cycle.

When the peak voltage of the applied A.C. voltage increases above the second and higher threshold voltage value of the device, as illustrated in FIG. 10, the device in addition to switching to the intermediate electrical

cal resistance condition illustrated by the curve 35 is substantially instantaneously switched along the curves 21 to the conducting condition illustrated by the curves 22, the device switching during each half cycle of the applied A.C. voltage. As the applied A.C. voltage nears zero so that the current through the device falls below the minimum current holding value, the device switches along the curve 23 from the low electrical resistance condition to the high electrical resistance condition illustrated by the curve 20, this switching occurring near the end of each half cycle.

For a given configuration of the device, whose electrical characteristics are illustrated in FIGS. 8 to 10, the high electrical resistance may be about 1 megohm, the intermediate electrical resistance about 500 K, and the low resistance about 10 ohms, the first threshold voltage value may be about 15 volts and the second threshold voltage value about 20 volts, and the voltage drop across the device in the low resistance conducting condition may be less than 1 volt, and the switching times may be in nanoseconds or less. It has been found that where ZrO_2 , and sometimes Al_2O_3 , are used as the refractory powder particles these double switching actions may be obtained.

While for purposes of illustration several forms of this invention have been disclosed, other forms thereof may become apparent to those skilled in the art upon reference to this disclosure and, therefore, this invention is to be limited only by the scope of the appended claims.

We claim:

1. The method of making a semiconductor element of a current controlling device for an electrical circuit including a semiconductor element and electrodes in low electrical resistance contact therewith, wherein said semiconductor element has a threshold voltage value and a high electrical resistance to provide a blocking condition for substantially blocking current therethrough, and wherein said high electrical resistance in response to a voltage above said threshold voltage value substantially instantaneously decreases between the electrodes to a low electrical resistance which is orders of magnitude lower than the high electrical resistance to provide a conducting condition for substantially conducting current therethrough, said method comprising, substantially individually coating high electrical resistance refractory powder particles with a thin solid coating of substantially VO_2 within a molar percent range of about 5 to 25% of substantially VO_2 , and forming said semiconductor element from said substantially VO_2 coated refractory powder particles.

2. The method as defined in claim 1 further comprising, reducing V_2O_5 to substantially VO_2 while individually coating the high electrical resistance refractory powder particles with the solid coating of substantially VO_2 .

3. The method as defined in claim 1 further comprising, mixing V_2O_5 powder particles with high electrical resistance refractory powder particles within a molar percent range of about 5 to 25% of V_2O_5 , and heating said mixture in a reducing atmosphere to a temperature between the melting point of V_2O_5 and the melting point of VO_2 to melt the V_2O_5 powder particles and form substantially VO_2 and individually coat the refractory powder particles with said thin solid coating of substantially VO_2 .

4. The method as defined in claim 1 further comprising, mixing V_2O_5 powder particles and V_2O_3 powder particles in substantially equal molar percent with high electrical resistance refractory powder particles within a molar percent range of about 5 to 25% of said V_2O_5 and V_2O_3 , and heating said mixture in a substantially inert atmosphere to a temperature between the melting points of V_2O_5 and V_2O_3 and the melting point of VO_2 to melt the V_2O_5 and V_2O_3 powder particles and form substantially VO_2 and individually coat the refractory particles with said thin solid coating of substantially VO_2 .

5. The method as defined in claim 1 further comprising, forming a V_2O_5 sol having charged V_2O_5 particles colloidally suspended therein, mixing high electrical resistance refractory powder particles with said V_2O_5 sol for attracting the charged V_2O_5 particles from said V_2O_5 sol to the surfaces of said refractory powder particles to provide the same with a thin coating of V_2O_5 , and drying and heating said mixture in a reducing atmosphere to reduce the V_2O_5 to substantially VO_2 and individually coat the refractory powder particles with said thin solid coating of substantially VO_2 .

6. The method as defined in claim 5 further comprising, suspending V_2O_5 in water and mixing with H_2O_2 to form a liquid having peroxyvanadates in solution in the water, boiling the solution to decompose the peroxyvanadates back to V_2O_5 to form the V_2O_5 sol having the charged V_2O_5 particles colloidally suspended therein.

7. The method as defined in claim 1 wherein said high electrical resistance refractory powder particles comprise SnO_2 , SiO_2 , Al_2O_3 , ZrO_2 or TiO_2 .

8. The method as defined in claim 1 further comprising, compacting said substantially VO_2 coated refractory powder particles into a pellet to form said semiconductor element.

9. The method as defined in claim 1 further comprising, mixing said substantially VO_2 coated refractory powder particles in a high electrical resistance carrier with said coated particles substantially in contact to form said semiconductor element.

10. The method as defined in claim 9 wherein said carrier is a paint.

11. The method as defined in claim 9 wherein said carrier is a glass.

* * * * *