

Dec. 9, 1969

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3,483,110

PREPARATION OF THIN FILMS OF VANADIUM DIOXIDE

Filed May 19, 1967

FIG. 1

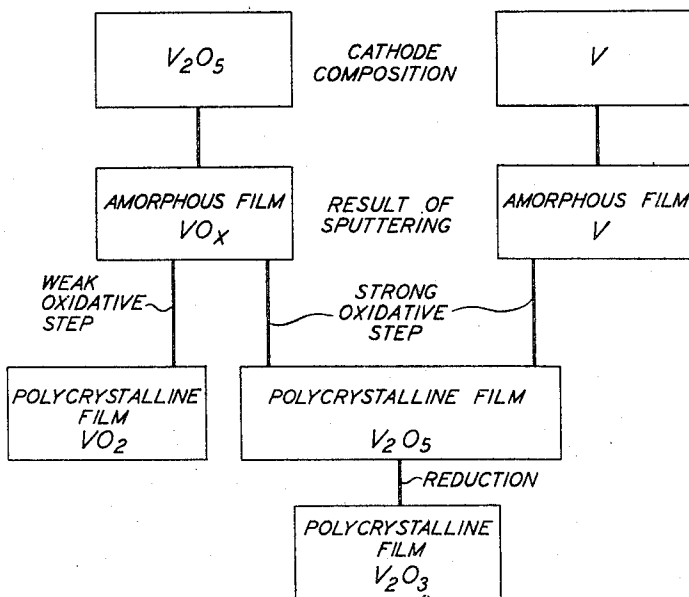
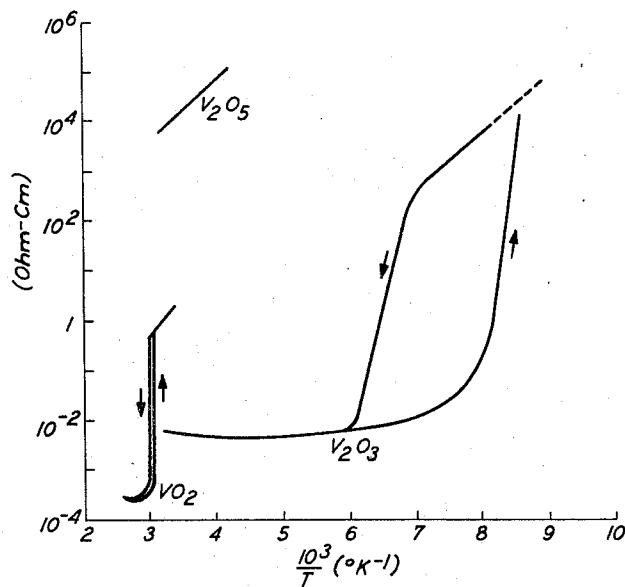


FIG. 2



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PREPARATION OF THIN FILMS OF VANADIUM
DIOXIDE

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Filed May 19, 1967, Ser. No. 639,902

Int. Cl. C23c 15/00

U.S. Cl. 204—192

3 Claims

ABSTRACT OF THE DISCLOSURE

A method has been found for making thin films of VO_2 that possess the essential metal-semiconductor phase transition exhibited by the single crystal forms, and that do not suffer deterioration under repeated cycling through the transition. The process involves the steps of sputtering with a V_2O_5 cathode to produce a film which is then oxidized to the desired oxidation state.

This invention relates to a process for making thin films of various vanadium oxides and to the products produced in accordance with the process.

BACKGROUND OF THE INVENTION

Recent interest has been shown in several materials which are able to undergo a metal-semiconductor phase transition at a characteristic temperature. Accompanying the transition are abrupt and substantial changes in various properties of the material, such as changes in its electrical resistance, light reflectance, etc. Devices which make use of these changes have been devised. Exemplary of those devices which take advantage of the abrupt change in resistance are switching devices as described in U.S. 3,149,298, issued to E. T. Handelman. Other devices, such as optical modulators and display devices, utilize the change in reflectance that occurs as the material passes through its transition temperature to modulate or alter some characteristic of impinging light.

Among the materials which possess such a phase transition characteristic are various vanadium oxides, for example, vanadium dioxide (VO_2) and vanadium sesquioxide (V_2O_3). It is important that these materials be in a form that is compatible with the modern planar device technology that is revolutionizing the electronics field. At present, however, these vanadium compounds are provided only as single crystals and not in the form of thin films for planar devices. Moreover, when single crystals of some phase transition materials are repeatedly cycled through the transition temperature, a "fracture" phenomenon often occurs causing a breakdown of the material, thus possibly imposing limits on the useful life of any device incorporating them.

SUMMARY OF THE INVENTION

In accordance with the present invention a method has been found for making thin films of VO_2 and V_2O_3 that possess the essential phase transition property exhibited by the single crystal forms, and that do not suffer deterioration under repeated cycling through the transition temperature.

In one form, the process involves the steps of sputtering a V_2O_5 cathode in an inert atmosphere in the presence of a desired substrate to produce an amorphous film of a composition VO_x , where x is greater than 1.5 but less than 2, and then either weakly oxidizing the film to end-product VO_2 , or strongly oxidizing the film to V_2O_5 and then reducing the V_2O_5 so produced as a V_2O_3 end-product.

Alternatively, a vanadium cathode can be sputtered in an inert atmosphere in a similar manner to provide a

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polycrystalline vanadium film which then is oxidized to V_2O_5 and then reduced to V_2O_3 .

Although the initial VO_x film is amorphous, the VO_2 , V_2O_3 and V_2O_5 films produced in accordance with the inventive method are made polycrystalline during the oxidative and/or reductive steps utilized.

DESCRIPTION OF DRAWING

The invention will be further described and particularized in the following detailed description in conjunction with the accompanying drawing in which:

FIG. 1 is a flowsheet presentation of the inventive process steps; and

FIG. 2 is a graph of the resistivity (ohm-cm.) vs. reciprocal temperature ($^{\circ}\text{K}^{-1}$) for VO_2 , V_2O_3 and V_2O_5 films produced by the inventive process.

DETAILED DESCRIPTION

As indicated by the flowsheet description of FIG. 1, the process of the invention can provide the vanadium oxides noted, VO_x , VO_2 , V_2O_3 , and V_2O_5 . Of course, thin films of VO_2 and V_2O_3 are especially of interest because of their phase transition characteristic and resistance to recycling fracture.

Conventional cathodic sputtering apparatus may be used in carrying out the invention. By way of example only, the following briefly sets forth the system used.

The cylindrical cathode of either V_2O_5 or V was 3 cm. in diameter and 3 cm. long. The vacuum system used was an all metal, sputter-ion pumped station with a water-cooled cylindrical reaction chamber 10 cm. in diameter and 15 cm. long. The cathode-to-anode spacing was 2 to 3 cm., although other spacings would be acceptable. The pressures used were of the order of 10μ to 300μ , although these can be extended to 1000μ with satisfactory results.

The effect of pressure on the sputtering operation is well known in the art. Increasing the pressure results in greater deposition rates due to the large number of bombarding ions present. However, at high pressures (relative to a perfect vacuum), the current flow obtained reaches undesirable limits. The lowest tolerable pressure is that which results in the smallest deposition rate that is economically acceptable. Operating pressures were established by evacuating the reaction chamber to 10^{-7} to 10^{-9} torr and backfilling with argon or other inert gas or mixtures thereof to reach the desired operating pressure. The cathode density should be adjusted to within the range 0.1 to 10 ma./cm.², the lower limit providing an adequate deposition rate, and the higher limit establishing a practical maximum to avoid short cathode life. Typical voltages to meet this requirement are from several hundred to a few thousand volts. Substrate temperatures may vary from 100°C . to 500°C . with the quality of the deposited film improving somewhat at the higher temperatures. Preferably, greater temperatures are not used in order to avoid damage to the film or substrate.

The cathode material that is sputtered can form a thin film on a variety of substrates; by way of example, films of VO_x and V have been successfully deposited on single crystal sapphire, amorphous glass, Si_3N_4 and Ta_2O_5 . The thicknesses of the films produced ranged from 200 to 6000 Å.

Substrate temperatures are not critical, and temperatures within 100 to 500°C . are convenient. With a cathode of V_2O_5 , a thin film of amorphous vanadium oxide is produced which has a composition VO_x where x is greater than 1.5 but less than 2. It is theorized that the V_2O_5 results in $\text{V}_2\text{O}_3 + \text{O}_2$ and that an amount of oxygen associates with the V_2O_3 to provide a stoichiometric composition for the film between V_2O_3 and VO_2 . The VO_x film can be converted either to VO_2 or V_2O_5 or V_2O_3 by

suitable post-deposition treatment involving oxidation and/or reduction in open tube furnaces.

The just-described effect of oxygen on the stoichiometry of the film is, of course, more extensive when large amounts of oxygen are present during sputtering. It is found that if oxygen is present in an amount greater than about 50 percent (by volume), the VO_x composition noted is not reproducibly deposited. Accordingly, some precaution is taken to minimize this effect. Spectral grade inert gas is preferred, as is a procedure which bleeds gas from the sputtering chamber, from time to time, to remove oxygen produced during sputtering. In addition, baking the chamber at a few hundred degrees centigrade prior to backfilling with inert gas removes various impurities from the chamber walls that could possibly introduce unwanted gaseous species into the system.

If VO_2 is desired, the VO_x film is contacted with an oxidizing atmosphere of water vapor which is found not to strongly oxidize the film to an oxidation state higher than VO_2 . Optimum results are obtained at a furnace temperature of 400–500° C. with contact maintained for about 4 hours. Other weak oxidants could also be employed to achieve a VO_2 composition.

On the other hand, V_2O_5 is obtained with stronger oxidants, for instance by an oxygen-rich atmosphere. For this purpose a 10% or greater O_2 mixture proves excellent, at a furnace temperature optimally at 450–550° C. for about 4 hours. The amount of oxygen is not critical to obtaining the desired end product, but secondary factors such as the rate of reaction depend on the oxygen concentration. The greater the oxygen content the more rapid the oxidation. The V_2O_5 film produced is characteristically yellowish and polycrystalline.

Alternatively, V_2O_5 is produced by sputtering a vanadium cathode to obtain a polycrystalline vanadium film that is typically black. The same sputtering conditions as described for V_2O_5 are applicable. The same post-deposition treatment just described for producing V_2O_5 from VO_x is also operable on the vanadium film to yield V_2O_5 .

It was not found possible to obtain V_2O_3 films by direct treatment of VO_x or V films with oxidants alone. Apparently the tendency is for these lower states to reach a vanadium pentoxide equilibrium rather than an intermediate V_2O_3 state. However, V_2O_3 is obtainable from a V_2O_5 film, regardless of whether it is produced by sputtering with a cathode of V_2O_5 or V, by contacting it with a reducing atmosphere, such as "wet" hydrogen that has been saturated with water vapor (room temperature), while in a furnace at about 500–600° C. for about 1 hour. This reductive step takes considerably less time than the oxidative steps above described, indicating the relative ease with which the reduction step takes place (less active reductants would take longer). It was not possible, however, to reduce V_2O_5 to the intermediate VO_2 .

FIG. 2 shows the resistivity vs. reciprocal temperature characteristics for the thin films of interest. The arrows indicate the direction of change.

Thin films of V_2O_5 exhibit only the properties of a semiconductive material over the temperature range studied. The VO_2 and V_2O_3 films, however, clearly show the phase transition from the semiconductor to the metal state which accompanies change in temperature through the transition temperature. The VO_2 shows a narrow hysteresis at about 65° C., which compares very favorably with the transition temperature for single crystal VO_2 . Films of V_2O_3 exhibited an abrupt transition to the metal state at about –110° C., with a transition back to the semiconductor state at about –145° C.

The resistance of these films to fracture was checked by cycling the VO_2 samples from room temperature to about 100° C., and by dipping the V_2O_3 samples in and out of liquid nitrogen. The samples underwent repeated resistance changes of $>10^3$ ohms for VO_2 and $>10^7$ ohms for V_2O_3 . A point-by-point measurement after cycling did not reveal any change in performance.

The invention has been described with reference to particular embodiments and examples thereof, but it is intended that variations therefrom which basically rely on the teachings of the invention are to be considered as within the scope of the description and the appended claims.

What is claimed is:

1. A process for making a thin film vanadium oxide comprising the steps of sputtering with a cathode of a composition consisting essentially of V_2O_5 onto a substrate heated to a temperature in the range from 100 to 500° C., in an atmosphere consisting essentially of inert gas and up to 50 percent by volume oxygen at 10 to 1000 μ , thus forming an amorphous film, and contacting said amorphous film with a weakly oxidizing atmosphere for a time sufficient to form a polycrystalline VO_2 film.

2. The process of claim 1 wherein said amorphous film is contacted with water vapor at 400 to 500° C.

3. The polycrystalline VO_2 film produced in accordance with the process of claim 1.

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U.S. Cl. X.R.

23—21, 140; 117—201; 148—6.3; 252—518; 338—306