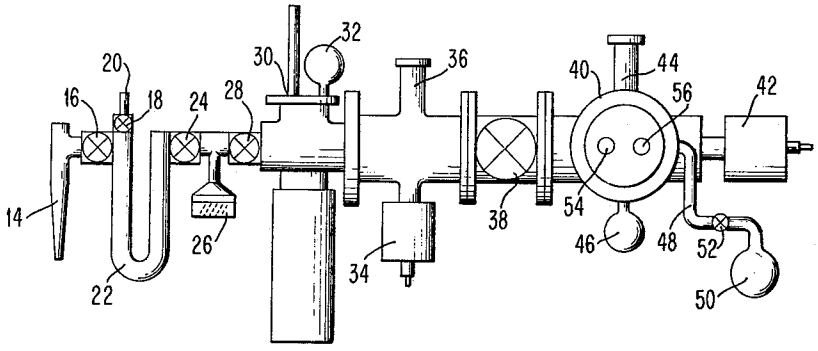
April 16, 1963 H. L. CASWELL 3,085,913

VACUUM EVAPORATION METHOD

Filed Oct. 3, 1960 2 Sheets-Sheet 1

FIG. 1



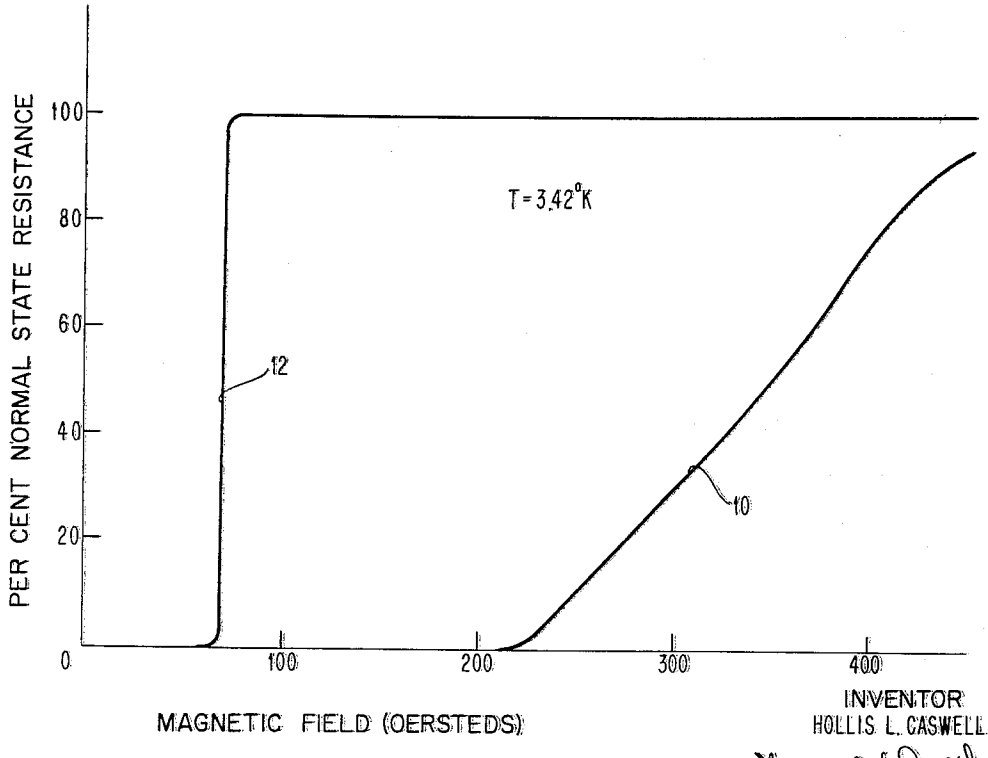


FIG. 2

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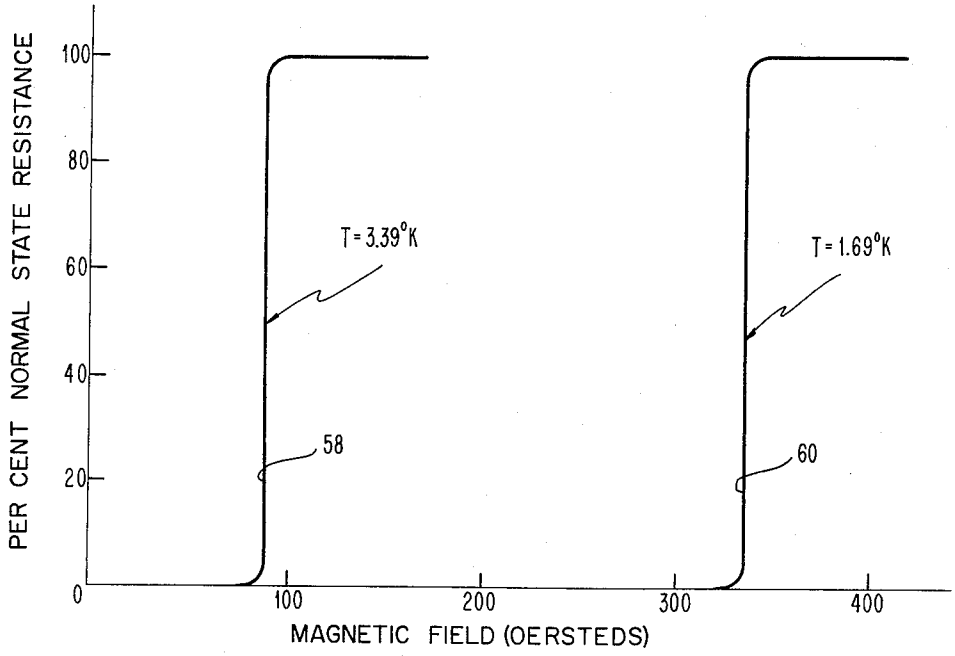


FIG. 3

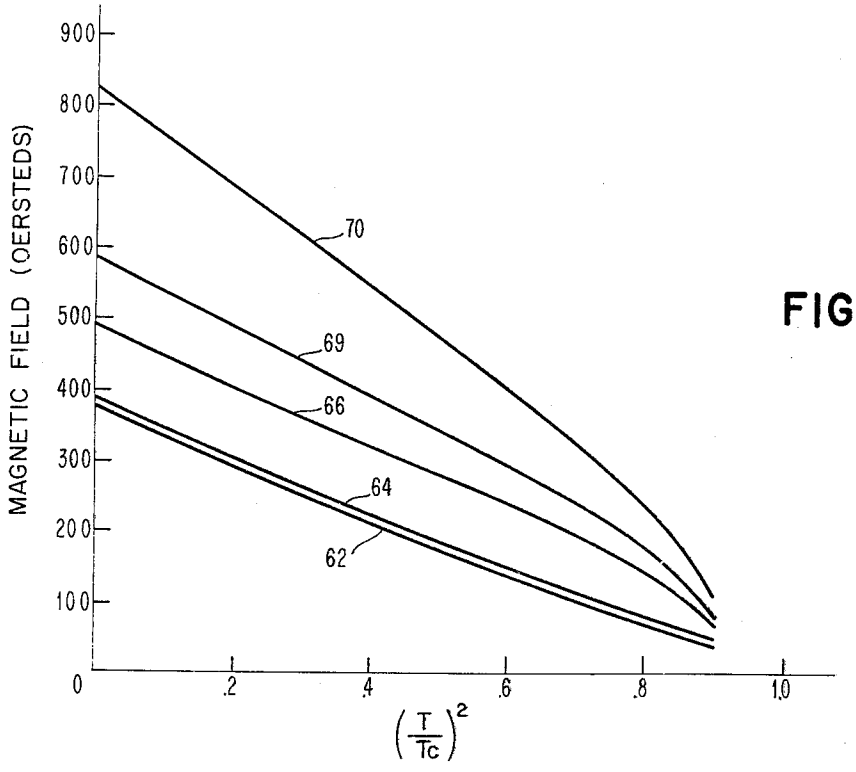


FIG. 4

United States Patent Office

3,085,913
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VACUUM EVAPORATION METHOD

Hollis L. Caswell, Poughkeepsie, N.Y., assignor to International Business Machines Corporation, New York, N.Y., a corporation of New York

Filed Oct. 3, 1960, Ser. No. 59,934
11 Claims. (Cl. 117—212)

This invention relates to a method of evaporating materials within a vacuum and more particularly to a method of evaporating materials within a vacuum to obtain thin films having controllable and reproducible characteristics.

Vacuum deposition of materials onto a substrate has been employed in many fields to produce a large variety of articles. Generally, the methods of the prior art consist essentially of heating a coating material in a vacuum and directing the vapors therefrom onto the article or substrate to be coated. Further, these directed vapors may flow through a pattern defining mask to obtain a predetermined geometry of deposited material upon the substrate. Recently, because of advances of the state of the art in many fields, including, by way of example, magnetics and superconductors, there has arisen the need of obtaining extremely thin film coatings having characteristics with a degree of uniformity greater than previously possible.

It has been found that the electrical properties of evaporated coatings or films may exhibit a lack of reproducibility in the results attained. Films evaporated under apparent identical conditions have exhibited a wide range of characteristics. The potentiality of utilizing evaporated thin film devices fabricated from magnetic or superconductive materials in high speed computers has stimulated further interest in evaluating the role various parameters play in determining the characteristics of evaporated thin films. It has been found that one important parameter in determining these characteristics is the magnitude of the vacuum in which the evaporation occurs. In general, the majority of the evaporations, wherein reproducibility of results was not generally obtained, were performed at pressures in the 10^{-6} to 10^{-5} mm. Hg range within systems evacuated by the well known oil diffusion pumps. In copending application, Serial No. 844,754, filed October 6, 1959, and now Patent No. 3,036,933, on behalf of Hollis L. Caswell and assigned to the assignee of this invention, there is disclosed a novel vacuum evaporation method wherein, through a series of steps, the pressure within the system is reduced to about 10^{-10} mm. Hg and then, through a further series of steps, the pressure is maintained at about 10^{-9} mm. Hg during an evaporation operation. By means of this novel combination of steps, thin films having controllable and reproducible characteristics are obtained.

What has been discovered is a novel method of evaporating materials at a pressure in the range of 10^{-6} to 10^{-5} mm. Hg wherein thin films having controllable and reproducible characteristics are also obtained. By the method of this invention, which avoids both the time and difficulty required to attain an ultra high vacuum, reproducible thin films are obtained. Briefly, the method of the invention involves the selective pumping of particular ones of the residual gases within the vacuum system to less than predetermined partial pressures, as

determined by the rate of evaporation of the particular material to be deposited. By this method, the gaseous impurities which are most effective in influencing the actual characteristics of the deposited thin film are readily reduced to pressures where they no longer influence these characteristics, resulting in the deposited thin film then exhibiting the required controllable and reproducible characteristics. Further, the method of the invention provides deposited films having a more uniform cross-section. In general, films deposited through a pattern defining mask exhibit edge portions which are thinner than the major portion of the deposited film. This results from the well known shadowing effect provided by the mask as well as the surface mobility of the deposited molecules on the substrate. However, through the selective pumping according to the invention, these thinner edge portions are disconnected from the center portion of the film through the lack of nucleation sites normally provided by the particular gases interacting with the atoms of the evaporated material, which, according to the method of the invention, have been selectively pumped to low partial pressures.

It is an object of the invention to provide an improved vacuum evaporation method.

Another object of the invention is to provide a method of obtaining vacuum deposition of materials having controllable and reproducible characteristics without attaining an ultra high vacuum.

A related object of the invention is to provide a method of fabricating superconductive circuits having controllable and reproducible characteristics.

A further object of the invention is to provide a method of fabricating thin films which exhibit a degree of uniformity greater than previously possible.

Yet another object of the invention is to provide a vacuum evaporation method wherein selective pumping of particular gases is employed.

Still another object of the invention is to provide a method of fabricating thin films having reproducible characteristics determined by the interrelation of the partial pressures of the residual gases within the vacuum system and the rate of deposition of the evaporated material.

Yet another object of the invention is to provide a method of obtaining thin films of superconductive materials having controllable and reproducible characteristics without attaining an ultra high vacuum.

A still further object of the invention is to provide a method of fabricating reproducible thin film superconductive circuits in a conventional vacuum system.

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of a preferred embodiment of the invention, as illustrated in the accompanying drawings.

In the drawings:

FIG. 1 is a diagrammatical illustration of an apparatus used to evaluate the method of the invention.

FIG. 2 shows a transition between a superconducting and normal resistance state of superconductive thin films fabricated according to the prior art, as well as fabricated in an ultra high vacuum system.

FIG. 3 shows transitions as a function of temperature between the superconducting and normal resistance state

of a superconductive thin film fabricated according to the method of the invention.

FIG. 4 shows the critical field as a function of operating temperature for superconductive thin films containing various amounts of oxygen.

The method of the invention is best described as applied to the fabrication of thin film superconductive circuits, wherein it is desired to control and reproduce the electrical characteristics thereof. These characteristics include; the critical field, which is the magnetic field required to switch a superconducting conductor from the superconducting state to the resistive state; the critical self current, which is the maximum current a superconducting conductor can carry before this current itself destroys superconductivity; the slope of the transition curve between the superconducting and normal resistance states; and the thermal and magnetic time constants. When thin film superconductive circuits are employed in large scale devices, such as computers or the like, it is desirable that each of the above characteristics be accurately controlled within close limits. As an example, each of the gate conductors must have about the same critical field value to ensure selected gate conductors are in the resistive state when subjected to the magnetic field applied by associated control conductors. Since superconductor circuits, as distinct from the method of fabricating these circuits, form no part of the present invention, they will not be further described herein. For a review of these devices and circuits, reference should be had to Progress in Cryogenics, volume 1, pages 3 to 30, published in 1959 by Heywood and Company, Ltd., London, England.

Referring now to the drawings, FIG. 2 illustrates the transition between the superconducting and normal resistance state of a pair of thin superconductive films. Curve **10** of FIG. 2 shows a typical transition obtained from a tin film deposited at a pressure in the range 10^{-6} to 10^{-5} mm. Hg. When a small measuring current is used to detect resistance, as can be seen in curve **10**, a large increase in the applied magnetic field is required in order to obtain a complete transition between the superconducting and normal resistance state. Curve **12** shows the transition of a similar tin film deposited in an ultra high vacuum maintained at 10^{-9} mm. Hg. It can be seen that the transition between states of this film is essentially discontinuous, that is, for all values of magnetic field less than about 75 oersteds complete superconductivity is exhibited; for all values in excess of this applied field, complete normal resistance is attained. The transition curves of each of these thin films was obtained at a temperature of 3.42° K. Further, although curve **12** is representative of all the films deposited in an ultra high vacuum, it should be noted that curve **10** is not representative of all films deposited at the higher pressures. At pressures in the range of 10^{-6} to 10^{-5} mm. Hg, films have been obtained which also exhibit an abrupt transition between states as well as films in which complete resistance is not exhibited even though the applied magnetic field exceeds 600 oersteds. From FIG. 2, it should be understood that the speed of switching between states of the film exhibiting a characteristic shown by curve **10** is necessarily longer than the switching speed of a film exhibiting the characteristic of curve **12** due to the large change in the applied magnetic field. Additionally, since the abrupt transition between states of a film having a characteristic shown by curve **12** occurs at a lower value of applied magnetic field, this film also inherently exhibits a more rapid speed of switching with equal control characteristics. However, as is next described, films deposited at a pressure in the range of 10^{-6} to 10^{-5} mm. Hg, according to the method of the invention, also exhibit the transition characteristics exemplified by curve **12** of FIG. 2.

The method of the invention may be practiced with various types of apparatus. FIG. 1 discloses in schematic form an apparatus which has satisfactorily been employed to obtain the advantages of the method of the invention, by way of example. This apparatus is essentially that disclosed and described in detail in the hereinbefore referenced patent and, as mentioned above, is capable of attaining a system pressure of 10^{-10} mm. Hg and of maintaining a system pressure of 10^{-9} mm. Hg during an evaporation operation. Since the method of this invention requires a system pressure of only 10^{-6} to 10^{-5} mm. Hg, all of the components shown in FIG. 1 are not required and their functions are briefly discussed in outline form. The apparatus of FIG. 1 includes a water aspirator **14** operable as a roughing pump, which is connected to the system by a valve **16**. A valve **18** serves to connect the system to a source of high purity nitrogen gas (not shown) through tubing **20**. A liquid nitrogen trap **22** is effective to prevent water vapor from aspirator **14** from entering the system and is selectively isolated from the system by a valve **24**. An absorbent pump **26** is operable as an auxiliary roughing pump and is connected to the system by means of a valve **28**. A liquid helium pump **30** having a first ionization gauge **32** attached thereto further reduces the system pressure below that obtainable through the combination of roughing pumps **14** and **26**. Next, a first ion-getter pump **34** cooperates with pump **30** in the further reduction of pressure. Connected opposite pump **34** is a first mass spectrometer **36**. A large bakeable valve **38** is operable to isolate the series of preliminary pumps **14**, **26** and **30**, **34** from a vacuum chamber **40**. Chamber **40** has attached thereto an ion-getter pump **42**, a second mass spectrometer **44**, a second ionization gauge **46**, and a tubing **48**. Tubing **48** connects to a hydrogen reservoir **50** through a calibrated valve **52**. Additionally connected through a surface of chamber **40** are a liquid nitrogen trap **54** and a substrate temperature controller **56**. Further, located within chamber **40** are the necessary components for thermal deposition of materials onto a substrate which include a substrate holder, a mask holder, evaporation source structures, shutters and electrical heaters, which may be those illustrated in detail in the above referenced patent, by way of example, or any of the well known substitutes therefor.

Before discussing the general theory and results of the method of the invention, a specific illustration of the evaporation of thin superconductive film of tin is first described to afford a basis of understanding the invention. As is discussed in detail in the specific illustration next described, thin superconductive films of tin having controllable and reproducible characteristics are fabricated by evaporating the superconductive material onto a substrate at a system pressure in the range of 10^{-6} to 10^{-5} mm. Hg provided selective pumping is employed to reduce the partial pressures of oxygen, water vapor, and carbon dioxide to predetermined values. Referring now to FIG. 1, water aspirator **14** is operated to reduce the pressure within chamber **40** from atmospheric to about 10 mm. Hg. At this time, valve **24** is closed and absorbent pump **26** is cooled with liquid nitrogen reducing the pressure to 10^{-3} mm. Hg. Valves **28** and **38** are next closed and ion-getter pump **42** is placed in operation. Additionally, pump **54** may also be cooled with liquid nitrogen to obtain a higher pumping speed. Alternatively, pump **42** is replaceable by a well-trapped oil or mercury diffusion pump but, as will be discussed hereinafter, it is preferred to use an ion-getter pump or an ion discharge of some type to provide more positive cleanup action of the surfaces within chamber **40** and particularly the substrate included therein. Pump **42** continues operation for a time sufficient to reduce the pressure within chamber **40** to about 10^{-5} mm. Hg. At this time, the substrate is subjected to a high temperature bakeout at about 400° to 450° C. for three hours to reduce the adsorbed water vapor thereon. The substrate is then cooled to room temperature and, next, a titanium getter is evaporated to selectively reduce the partial pressure of oxygen. If

an ion pump having a titanium evaporation source is employed, it is not necessary to use a separate titanium getter. This gettering step in the method of the invention is effective to selectively reduce the partial pressure of oxygen. The next step in the method is to fill trap **54** with liquid nitrogen to selectively reduce the partial pressure of carbon dioxide as well as to aid in the reduction of the partial pressure of water vapor. At this time, valve **52** is opened to introduce a flow of hydrogen at a controlled pressure of about 10^{-5} mm. Hg. This step in the method is included, since hydrogen is additionally effective to reduce the partial pressure of oxygen through the formation of water vapor on the heated filaments and sources and, further, as particularly described, in copending application Serial No. 57,331, filed September 20, 1960, on behalf of I. Ames et al. and assigned to the assignee of this invention, a portion of the hydrogen is ionized by the ion-getter pump and is thereby effective to additionally clean the substrate and the walls of chamber **40**. At the conclusion of these steps, mass spectrometer **44** indicates the partial pressure of oxygen to be less than 10^{-7} mm. Hg, the partial pressure of water to be less than 10^{-6} mm. Hg, the partial pressure of carbon dioxide to be less than 10^{-7} mm. Hg, and the partial pressure of all the remaining gases in the system to each be less at 10^{-5} mm. Hg, while ionization gauge **46** indicates a total system pressure between 10^{-6} to 10^{-5} mm. Hg. The final step in the process is then to deposit the tin through the mask onto the substrate at an evaporation rate between 50 and 100 Angstrom units per second.

Referring now to FIG. 3, there is shown the transitions as a function of temperature between the superconducting and resistive state of a thin tin film fabricated in accordance with the above-described steps. Transition curve **58** was obtained at a temperature of 3.39° K. and curve **60** was obtained at a temperature of 1.69° K. It is seen that the transition between states is essentially abrupt, that is, the film exhibits complete superconductivity below the critical field value and complete normal resistance for an applied field in excess of this value. Although the transition illustrated by curve **60** in FIG. 3 occurs at an applied field of about 330 oersteds, which is relatively large as compared with curve **12** of FIG. 2 by way of example, this results solely from the reduced operating temperature, it being understood by those skilled in the art that the critical magnetic field increases as the operating temperature decreases, and, additionally, it should be noted abrupt transitions are more difficult to obtain at lower temperatures. For a more complete evaluation of thin films fabricated according to this invention, reference is now made to FIG. 4 which indicates the critical magnetic field as a function of temperature for films fabricated at an ultra high vacuum, for films fabricated according to the method of the invention, and for films fabricated in the presence of controlled amounts of oxygen. A similar family of curves is obtainable for most other gases, particularly for water and carbon dioxide, wherein diversions, which are less than that illustrated in FIG. 3, from the characteristics exhibited by films deposited at an ultra high vacuum are also exhibited. Curve **62** was obtained from a film deposited in an ultra high vacuum. Curve **64** was obtained from a film deposited at a pressure between 10^{-6} and 10^{-5} mm. Hg according to the method of the invention. It is seen that these curves follow each other almost point for point, indicating that the magnetic transitions of films fabricated according to the method of this invention are similar to those of films fabricated in an ultra high vacuum. Further, in FIG. 4, curve **66** indicates the characteristic for a film deposited in the presence of a controlled partial pressure of oxygen such that the ratio of oxygen molecules to the tin atoms striking the substrate was maintained at 3%. Curves **69** and **70** indicate the further diversion from the characteristic of the film deposited at ultra high vacuum when the ratio of oxygen molecules to tin atoms is increased to 6 and 9%, respectively. From similar families of curves obtained for the other gases present within conventional vacuum systems, limits are also obtained for the ratio of the particular gas molecules to tin atoms, hereinafter defined as K, which are listed in Table I and are further discussed in the portions of this description which follows.

Table I

Gas:	Value of coefficient K
Oxygen	Less than 0.1%.
Water	Less than 1%.
Carbon dioxide	Do.
Nitrogen	Less than 200%.
Hydrogen	Do.
Carbon monoxide	Do.
Argon	Do.
Sum of all gases	Less than 300%.

In the fabrication of thin superconducting films, it was believed that the film characteristics were affected by the impurities contained therein. However, as shown in copending application, Serial No. 861,038, and now U.S. Patent No. 2,989,716, filed December 21, 1959, on behalf of Andrew E. Brennemann et al., and assigned to the assignee of this invention, it is disclosed that thin superconductive films fabricated in conventional evaporators are characterized by a variation in the thickness which is concentrated in the edges of the film, removal of these edges being effective to provide superconductive circuit elements having controllable and reproducible characteristics. The selective pumping as taught by the method of this invention is also effective to cause the edges of the deposited film to be electrically disassociated from the major portion of the deposited film in the following novel manner. First, the substrates prior to being placed within the vacuum system are subjected to an extensive cleaning process which includes cleaning with ethyl alcohol in an ultrasonic cleaner, and further the substrate is subject to a high temperature bakeout within the vacuum system which is effective to desorb water vapor adhering thereto. Next, the partial pressures of water, oxygen and carbon dioxide are selectively reduced, and, additionally, the heavier hydrocarbon compounds are prevented from entering the system by preferably using an ion-getter pump or, alternatively, employing a well-trapped diffusion pump. In this manner, it has been found that these steps together are effected to prevent nucleation sites to be formed under the shadow of the mask thus causing it to be extremely difficult to form continuous films until the thickness of the edges is in excess of 2,000 Angstrom units in thickness. Since the thin films under consideration are in the order of 3,000 to 5,000 Angstrom units in thickness, the edge portions do not obtain a thickness sufficient to connect the thinner edges to the center portion of the deposit. However, in conventional systems evacuated to a pressure in the range of 10^{-6} to 10^{-5} mm. Hg, the partial pressures of oxygen, water and carbon dioxide have been reduced to about 10^{-6} mm. Hg and at this partial pressure K obtains a value of between 1 and 10%. With this value of K for each of these gases, nucleation sites are provided which allow the thinner edge portions, having a thickness between essentially 0 and approximately 500 Angstrom units, to become connected to the center portion of the film.

It should be noted that the coefficient K, which is the ratio of the molecules of a particular gas to the number of atoms of the material striking the substrate, is a function of both the partial pressure of the particular gas and the rate at which the material is evaporated and directed through the mask. This results since the number of molecules of the material striking the substrate is necessarily a function of the rate at which the material leaves the evaporation source which, by definition, is the evaporation rate. Additionally, the partial pressure of the gas is indicative of the number of molecules present within the system and, for the range of pressures being con-

sidered herein, the mean free path within a conventional system is determined by the dimensions of the system so that the number of gas molecules striking the substrate is therefore a function of the number of molecules present within the system. Thus, when increased evaporation rates are employed, higher partial pressures of the critical gases are allowable and, conversely, when lower deposition rates are employed, the partial pressures of the critical gases must be correspondingly reduced. However, the evaporation rate of the material should be high enough to obtain reasonable grain size in a deposited film and yet is preferably limited in rate in order to prevent "spitting" of the molten material as well as to limit the amount of outgassing from the evaporent. For this reason, a range of evaporation rates from 50 to 100 Angstrom units per second is generally preferred. Further, it is generally desirable to limit the partial pressure of any of the gases in the system to about 10^{-5} mm. Hg so that the condition referred to above, namely, that the mean free path of gas molecules within the system is determined by the dimensions of the system itself, results in order to obtain essentially uniform concentration of gas throughout the entire volume of the system and also, to prevent scattering of the evaporated material by the residual gas molecules.

From the above, it is seen that in order to obtain high purity superconductive thin films exhibiting sharp magnetic transitions which occur at controllable and predictable values of applied magnetic field it is not necessary to reduce the total pressure within a vacuum system to a very low value prior to the thermal evaporation of the superconductive material. Rather, it is only necessary at a conventional vacuum pressure, to reduce that partial pressures of several critical gases. Of the various gases, oxygen is the most detrimental in influencing the magnetic transitions and, therefore, must be selectively reduced to the lowest partial pressure. The next important of the various gases are water and carbon dioxide, which initially must be selectively pumped to partial pressures significantly lower than the total system pressure. It should be noted, however, that in order to obtain thin films having reproducible and controllable characteristics, the substrate surface upon which the material is deposited must be thoroughly celan and, additionally, subjected to a high temperature vacuum bakeout to reduce the water vapor content adhering thereto. Further, as in conventional vacuum technology, when an oil diffusion pump is employed to obtain the final system pressure, the partial pressures of the various hydrocarbon compounds entering the vacuum system from the diffusion pump must be maintained at reasonably low values of the order of 10^{-5} mm. Hg. Thus, it has been shown that by preferentially pumping predetermined critical gases and also employing a reasonable evaporation rate of the superconductive material, high purity superconductive thin films exhibiting sharp and predictable critical field transitions are obtained without employing an ultra high vacuum evaporator and expending the time necessary to attain an ultra high vacuum.

Additionally, the method of the invention may also be employed in the fabrication of thin films of other superconductive materials in order to obtain films having controllable and reproducible characteristics. By way of example, indium is an additional material useful in superconductive circuits. Since the steps of the method of obtaining thin indium films having controllable and reproducible characteristics are the same as the steps described above in detail to obtain tin films, they will not again be enumerated in detail. Selective pumping of oxygen to reduce the value of K therefore to less than 0.1% is effective to provide the desired films as with tin provided the partial pressures of the remaining residual gases are each about 10^{-5} mm. Hg. Further, the presence of water vapor and carbon dioxide does not influence the film characteristics or edge breakup as with tin.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

In the claims:

1. The method of forming a thin film of material by thermally evaporating said material through a pattern defining mask upon a substrate within a vacuum system comprising; reducing the total pressure within said system to about 10^{-5} mm. Hg, said total pressure being the sum of partial pressures of a plurality of residual gases; and then thermally evaporating said material at a constant rate after the partial pressure of selected ones of said plurality of residual gases has been reduced below a predetermined value to ensure that said deposited thin film of material has sharply defined edge portions as determined by said mask.

2. The method of forming a thin film geometric pattern of material upon a substrate within a vacuum system comprising; reducing the total pressure within said system to about 10^{-5} mm. Hg, said total pressure being the sum of partial pressures of a plurality of residual gases; further reducing the partial pressure of selected ones of said plurality of residual gases; and thermally evaporating said material onto said substrate at a predetermined rate through a pattern mask which defines said geometric pattern, said reduced partial pressures of said selected ones of said plurality of residual gases effective to render the thinner edge portions of said deposited material discontinuous from the center portion of said deposited material.

3. An improved method of forming a thin film of material by thermally evaporating said material through a pattern mask upon a substrate within a vacuum system comprising; reducing the total pressure within said system to about 10^{-5} mm. Hg wherein said total pressure is the sum of partial pressures of a plurality of residual gases within said system; further reducing the partial pressure of selected ones of said plurality of residual gases; and thermally evaporating said material onto said substrate at a rate dependent upon the partial pressures of said selected ones of said plurality of residual gases, said dependent rate effective to prevent the formation of nucleation sites by said selected ones of said plurality of residual gases.

4. The method of evaporating a material through a pattern defining mask and depositing said material onto a substrate within a vacuum system, said deposited material thereafter exhibiting controllable and reproducible electrical characteristics, which method comprises the steps of; evacuating said system to a predetermined pressure, said predetermined pressure being the sum of the partial pressures of residual gases within said system; and evaporating said material through said mask onto said substrate at a predetermined rate after the partial pressure of selected ones of said residual gases within said system have each been reduced to a value such that the ratio of arrival of molecules of each of these gases to the molecules of said material arriving at said substrate when said material is evaporated at said predetermined rate is less than 0.1%.

5. The method of forming thin films of a material upon a substrate within a vacuum system comprising the steps of; reducing the pressure of all gases within said system to a first value; further reducing the partial pressure of selected ones of said gases to a second value which is lower than said first value, and evaporating said material onto said substrate at a predetermined rate, said rate being effective to form said thin film before said reduced partial pressure of selected ones of said gases provide nucleation sites for said evaporated material.

6. The method of evaporating a thin film of super-

conductive material upon a substrate within a vacuum system comprising the steps of; reducing the total pressure within said chamber to about 10^{-5} mm. Hg; and evaporating said material onto said substrate at a predetermined rate after the partial pressure of residual oxygen within said system has been reduced to a value such that the ratio of arrival of oxygen molecules to the material molecules upon said substrate when the material is evaporated at said predetermined rate is less than 0.1% whereby said film exhibits a sharp magnetic transition between a superconducting and normal resistive state.

7. The method of evaporating a superconductive tin thin film upon a substrate within a vacuum system comprises the steps of; reducing the total pressure in said system to below 10^{-5} mm. Hg; reducing the partial pressure of oxygen to below 10^{-7} mm. Hg through the operation of a titanium getter; reducing the partial pressures of water vapor and carbon dioxide each below 10^{-6} mm. Hg by operating a liquid nitrogen cold trap; and evaporating said tin at a rate between 50 and 100 Angstrom units per second whereby said tin thin film exhibits a sharp magnetic transition between the superconducting and resistive states.

8. The method of evaporating a superconductive thin film upon a substrate within a vacuum chamber comprising the steps of; reducing the pressure within said chamber to less than 10^{-5} mm. Hg; subjecting said substrate to a temperature of about 400° C. for a time sufficient to desorb the major portion of water vapor adhering thereto; reducing the partial pressure of oxygen within said system to less than 10^{-7} mm. Hg; reducing the partial pressure of carbon dioxide and water vapor within said system each to less than 10^{-6} mm. Hg; and depositing a superconductive material upon said substrate at a predetermined rate whereby said deposited film exhibits a controllable and reproducible transition between the superconducting and normal resistance states.

9. The method of forming thin superconductive films within a vacuum chamber wherein the total pressure has been reduced to the 10^{-5} to 10^{-6} mm. Hg range and wherein the partial pressure of oxygen is less than 10^{-7} mm. Hg and the partial pressure of water vapor and carbon dioxide is each less than 10^{-6} mm. Hg by thermally evaporating a superconductive material in said chamber onto a substrate after said vacuum has been attained.

10. The method of forming a thin tin film having controllable and reproducible characteristics upon a substrate within a vacuum system comprising; reducing the partial pressure of oxygen within said system to less than 10^{-7} mm. Hg; reducing the partial pressure of water vapor and carbon dioxide within said system each to less than 10^{-6} mm. Hg; reducing the partial pressure of the remaining gases within said system each to less than 10^{-5} mm. Hg; and thermally evaporating said tin onto said substrate at a predetermined rate.

11. The method of forming a thin indium film having controllable and reproducible characteristics upon a substrate within a vacuum system comprising; reducing the partial pressure of oxygen within said system to less than 10^{-7} mm. Hg; reducing the partial pressure of the remaining gases within said system each to less than 10^{-5} mm. Hg; and thermally evaporating said indium upon said substrate at a predetermined rate.

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