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Greiner

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[45] Nov. 19, 1974

[54] **PROCESS FOR FORMING REACTIVE LAYERS WHOSE THICKNESS IS INDEPENDENT OF TIME**

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[22] Filed: **Mar. 19, 1971**

[21] Appl. No.: **125,993**

[52] **U.S. Cl.** ..... **204/192,** 117/106 A, 117/107, 117/201, 204/298

[51] **Int. Cl.** **C23c 13/00,** C23c 15/00

[58] **Field of Search** 204/192

[56] **References Cited**

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[57] **ABSTRACT**

A method for forming reactive layers on materials where the final thickness of the reactive layer is independent of time after an initial time period in which the final thickness is attained. Films are grown by a process, such as oxidation, and are removed simultaneously by a process, such as sputtering. The parameters of the growth process and removal process are initially fixed so that at a desired final thickness, the growth rate is equal to the removal rate. When this steady-state equilibrium is reached, the thickness of the reactive layer will remain constant, independent of time. The reactive layer can be grown to the desired thickness by this method, or a thicker layer can be reduced to a lesser final thickness by this method. Very small (less than 50A) films of excellent quality can be made.

27 Claims, 10 Drawing Figures

FIG. 1

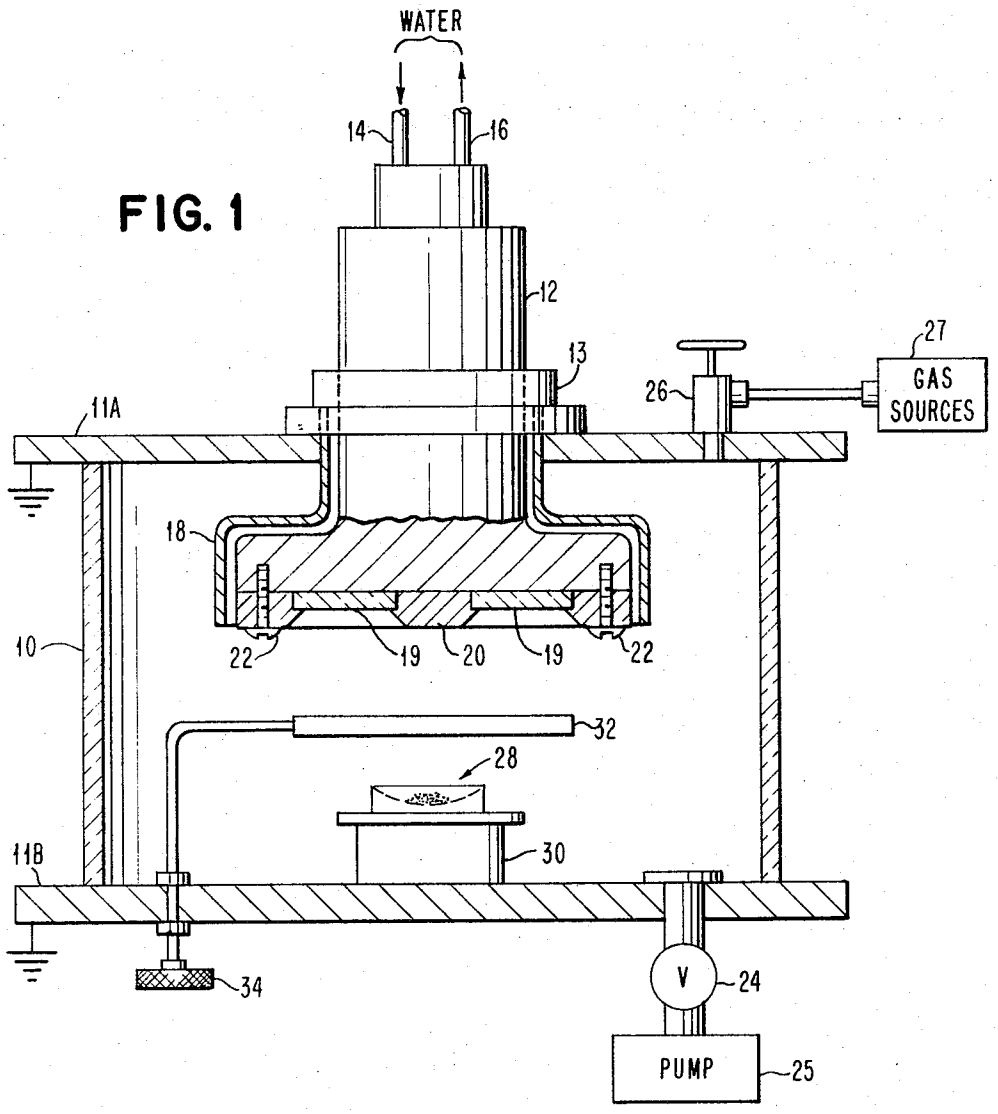


FIG. 2A

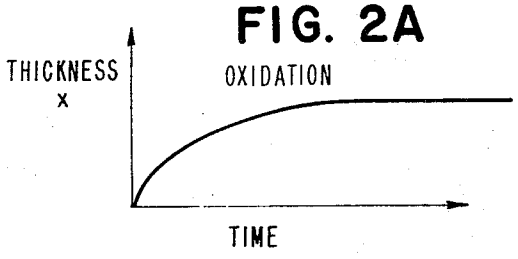


FIG. 2B

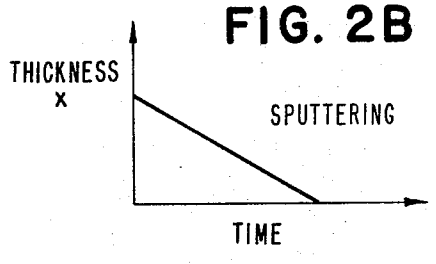
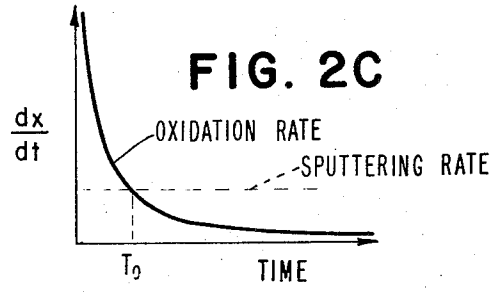


FIG. 2C



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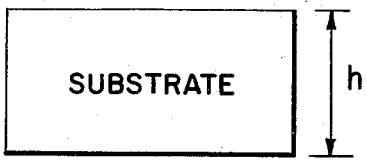
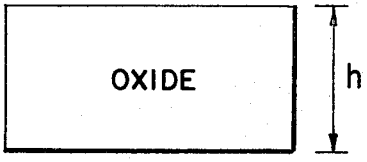
AGENT

FIG. 3A



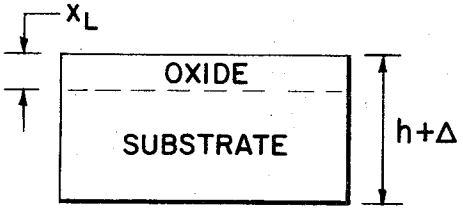
TIME T_1

FIG. 4A



TIME T_1

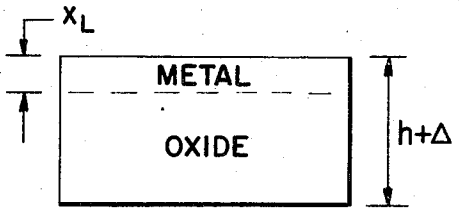
FIG. 3B



TIME T_2

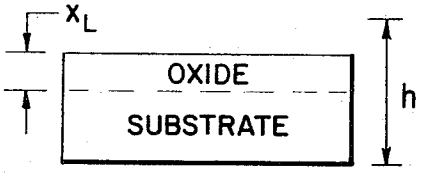
OXIDATION AND SPUTTERING RATES EQUAL

FIG. 4B



TIME T_2

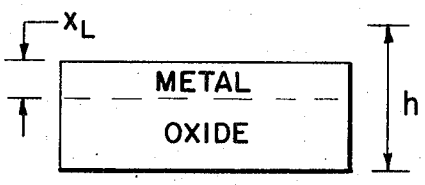
FIG. 3C



TIME T_3

OXIDATION AND SPUTTERING RATES REMAIN CONSTANT AND EQUAL

FIG. 4C



TIME T_3

PROCESS FOR FORMING REACTIVE LAYERS WHOSE THICKNESS IS INDEPENDENT OF TIME

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for forming reactive layers of desired thicknesses, and specifically to a method for forming reactive layers having reproducibly accurate final thicknesses which remain constant even if the method is continued further.

2. Description of the Prior Art

Reactive layers, such as oxides, nitrides, sulfides, etc. are useful in the production of many devices. For instance, Josephson junction devices use very thin (less than 50A) reactive layers as tunnel barriers between two superconducting electrodes. Generally, the base electrode is oxidized to form the tunnel barrier. Another device using reactive layers is a field effect device having an oxide insulator below its gate electrode.

Reactive layers are defined generally as layers formed on base materials and are combinations of the base material and other reactive materials. For instance, if lead is oxidized by oxygen species located adjacent to the lead substrate, a reactive layer of lead oxide will be formed on the lead substrate.

Many processes have been used for depositing reactive layers on metals and semiconductors. A review paper treating these processes if J. F. O'Hanlon, *Journal of Vacuum Science and Technology*, Vol. 7, No. 2, Page 330 (1969). This paper notes that plasma anodization has been used to produce oxide films where the samples to be anodized are located between the cathode and the anode. Both RF and DC discharges have been used.

The following references discuss many aspects of production of reactive films, some of which are very thin for particular use in Josephson junctions. These references describe thermal oxidation, evaporation, sputtering, and anodization.

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In the production of reactive layers, it is important that the thickness of the formed layers be reproducibly obtained over many cycles of the process. This is especially true if the films to be produced are very thin, as is the case with Josephson devices. Since the tunneling current in Josephson devices varies exponentially with the tunnel barrier thickness, small variations in thickness from one device to another can lead to serious problems when arrays are to be fabricated.

Another problem that occurs frequently in prior art methods for formation of reactive layers involves impurity incorporation in the growing film. Often, the substrate on which the reactive layer is to be produced is placed in the glow discharge between a cathode and an anode. Sputtering from the cathode occurs and often the cathode material finds its way to the target, even if shielding is used.

It is also important that the quality of the reactive film be good. It should be a very dense film having no pinholes or impurities therein which may cause problems such as electrical shorting in devices incorporating these films. In prior processes, ultra clean systems are required and the quality of the grown films was difficult to evaluate over a period of deposition ruins.

Prior methods for forming reactive layers do not provide good control of the final thickness of the layer. Generally the process is stopped after a certain amount of time, knowing that the thickness of the film would have an approximate value after a certain amount of time had passed. However, formation of very thin films (less than 50A) is difficult when the only control over thickness is the amount of time during which the process is allowed to continue. For instance, water vapor may be present in the system and may contribute additional oxygen ions. If an oxide film is being formed, the initial oxidation rate may be very high, so that the film achieves a thickness greater than that desired before the process can be terminated. In this situation, the quality of the film is apt to be inferior, in addition to its being too thick. The prior art methods do not have good thickness control, since the primary technique for obtaining thickness control is to slow the growth rate and then turn off the process after a period of time calculated to achieve a desired thickness.

Accordingly, it is a primary object of this invention to provide a process for growing reactive layers which is time independent.

Another object of this invention is to provide an improved process for growth of reactive layers, in which layers of any desired final thickness can be grown.

Still another object of this invention is to provide a process for growth of reactive layers in which the thickness of the grown layers is reproducibly constant during each deposition.

A further object of this invention is to provide a process for formation of reactive layers, where the thickness of the layers is uniform throughout the layer.

A still further object of this invention is to provide a time independent process for formation of reactive layers, even if the initial thickness of the reactive layer is greater than that desired.

Another object of this invention is to provide an improved process for formation of reactive layers which is time independent and which produces high quality reactive layers.

Still another object of this invention is to provide an improved process for formation of reactive layers which is time independent and easily controlled to provide reactive layers of any desired thickness, regardless of the cleanliness of the process environment system and the substrate used.

SUMMARY OF THE INVENTION

This method forms reactive layers on any substrates, such as semiconductors or metals. The layers formed include oxides, nitrides, sulfides, etc. A reactive species is brought into contact with the substrate and the reactive layer is formed thereon. While the layer is forming, another process occurs simultaneously which removes

the layer. After a period of time, a steady state equilibrium is produced at which the growth rate is equal to the removal rate. At this thickness, the reactive layers will maintain a constant thickness, independent of time.

In the particular case of an oxide film, a low power RF oxygen discharge can be used to form the oxide layer. A substrate is affixed to the cathode in the discharge and consequently will be both oxidized and sputtered during the process. If the oxidizing rate is initially larger than the sputtering rate, an oxide film will form. The oxide rate decreases as the oxide thickness increases because it is intrinisically a diffusion limited process. However, the oxide sputtering rate is independent of the thickness of the bombarded oxide. Therefore, if the oxidation rate is initially higher than the sputtering rate the oxide layer thickness will increase until the rate of oxidation becomes equal to the sputtering rate, at which time a steady state oxide thickness is attained.

Conversely, if an oxide film is present and the sputtering rate is initially higher than the oxidation rate, the oxide thickness decreases until the oxidation and sputtering rates become equal, or until the oxide is removed. The final thickness of the oxide layer will depend upon the equalization of the sputtering rate and the oxidation rate, both of which can be initially established to yield the desired final thickness at equilibrium.

As another alternative, an oxide layer can be reduced by a species such as hydrogen, which is present in the glow discharge. This will lead to production of a pure base material having a desired thickness established by the system parameters. For instance, a film of lead oxide can be reduced by bombardment of hydrogen ions, to produce a pure lead layer on the lead oxide, the pure lead layer having a constant final thickness determined by the system parameters.

This process is particularly attractive for formation of very thin films of constant thickness. Films less than 100A can easily be produced merely by setting the system parameters, which include (1) the temperature the substrate, (2) the RF power, (3) the pressure of the reactive species, and (4) the composition of the gaseous discharge. Some of these parameters affect the removal process (sputtering), while others have a greater effect on the growth process (oxidation). These can be set initially, and no dependency on other factors, such as impurity levels, is present. Once a steady state equilibrium is reached, the film thickness will remain constant and the process can be run for any length of time in order to provide high purity films having constant thickness.

In the preferred system, the substrates are placed on the cathode and an RF glow discharge is established between the cathode and an anode. The reactive species is introduced into the chamber containing the cathode and the anode, and a discharge is maintained by application of RF power between the cathode and the anode. The system parameters mentioned above are adjusted so that, at a desired final thickness, the deposition rate and the removal rate will be equal. Since the sample is placed on the cathode, deposition of cathode material on the sample can be eliminated, which is not the case if the substrate were placed in the glow discharge between the cathode and the anode. In addition to the contamination problem, systems in which the substrate is placed between the cathode and the anode produce films of varying thickness, since some sputtering may occur between the cathode and the substrate. In those systems, the final thickness is generally limited by the geometry of the system. Consequently, a process in which the substrate is placed on the cathode avoids these problems and yields films of constant thickness having minimal impurity contamination, and in which there is no deposit other than that from the intended source.

Since the solid state equilibrium is reached quickly in this process, good quality films are produced. This is a high energy process in which ions are propelled at the target, in contrast to the production of reactive layers by thermal processes. Further, since the reactive film is being removed at the same time it is formed, new reactive material is being constantly established. This means that any impure initial layer will be removed and, as the system becomes more clean, the quality of the grown layer will improve.

This method has another advantage in that the composition of the reactive film can be tailored by varying the composition of the discharge ambient. Regardless of the thickness required, chemically different reactive layers may be produced by incorporating different amounts of the reactive species in the gaseous ambient.

Because the substrate is placed on the cathode, there is nothing to perturb the discharge existing between the cathode and the anode. This leads to a process having greater control, resulting in uniform films of reproducible thickness. Since an equilibrium process is described, constant thickness independent of time can be produced continually. For manufacture of large arrays of devices and for reactive layer formations on a continuing basis, no danger exists that the thickness will change from one system to another and from one formation run to another. Thus the process is especially attractive for use in production lines where countless numbers of devices using reactive layers are produced.

Another advantage in the present method is that initial cleaning steps are not required. In conventional processes, a long initial discharge time is required to clean the system before deposition onto the substrate. With the present system impurities such as H_2O do not influence the quality of the final reactive layer. If the layer initially grows too thick due to the impurities, it will settle back to its desired final thickness when the rate of growth is equal to the rate of removal. Also, the initially produced impure film will be removed during the formation process, with the result that the film produced after steady state equilibrium is achieved will be very pure.

Although DC discharges can be used, RF discharges are preferred for growth of the reactive layers. Discharges can be sustained at lower pressures when RF power is used, as opposed to the higher pressures needed to sustain the discharge when DC power is used. This makes it more easy to remove adsorbed particles on the reactive layer before deposition of a subsequent layer. For instance, if an oxide layer is produced on a base electrode and it is desired to produce a counter electrode on this oxide layer, removal of adsorbed oxygen atoms from the reactive layer before deposition of the counter electrode is more simple if an

RF discharge had been used to form the reactive layer.

The prior art does not teach that a growth process can be balanced with a removal process to form reactive layers having any desired thickness, where the final thickness is independent of time. While the art does suggest that terminal thicknesses can be the result of various processes, nowhere is it suggested that any desired thickness can be achieved by initially selecting system parameters to force competing processes to be equal at that thickness. It has also been known that processes such as oxidation produce films of limiting thickness, in this case due to the diffusion limited nature of the oxidation process. However, it is believed that applicant is the first to teach that competing processes should be used to produce films of any desired thickness, and that it makes no difference whether the film is grown from zero thickness or is reduced from a thickness greater than that desired. The process enables reproducible formation of films having any desired thickness, totally independent of the time of formation once steady state equilibrium is achieved. Of course, the time period for achieving steady state equilibrium will vary depending upon the thickness desired, and the initial setting of the system parameters.

While sputtering and deposition within the sputtering apparatus is a particularly useful embodiment, other growth and removal processes can be used according to this invention. For instance, the removal process can be achieved by an apparatus separate from the growth process. An example of this is the use of an ion beam to etch away the depositing reactive layer. Another combination of growth and removal processes may be a liquid anodization growth process (for example to oxidize a substrate), in which the electrolyte dissolves some of the grown layer into solution, thereby removing it. Consequently, it is apparent that the growth and removal processes can be separate, independently adjustable processes using the same or separate means for performing those processes. Also, the rates of the growth and removal processes can be varied at any time during the formation of the reactive layer or they can initially be set to reach steady state equilibrium at some thickness of the reactive layer without further adjustment.

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

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of an RF sputtering apparatus suitable for carrying out the present method.

FIG. 2A is a plot of thickness of the formed reactive layer as a function of time for a growth process, in this case oxidation.

FIG. 2B is a plot of the thickness of the reactive layer as a function of time for a removal process, in this case sputtering.

FIG. 2C is a plot of the rates of the growth process (oxidation) and the removal process (sputtering) as a function of time.

FIGs. 3A, 3B, and 3C illustrate the growth of a reactive layer on a substrate with time, the reactive layer being conveniently shown as an oxide.

FIGS. 4A, 4B and 4C show the production of a pure layer from a reactive layer, where the reactive layer is conveniently shown as an oxide and the pure layer is conveniently shown as a metal forming a constituent of the oxide.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This method employs simultaneously occuring growth processes and removal processes in order to obtain good quality, reproducibly uniform reactive layers on various substrates. In particular, the method will be described by describing the formation of a controllable oxide layer on a substrate. It should be understood that other reactive layers, such as nitrides, sulfides, etc. can be formed on a base material (substrate). Whatever the species comprising the reactive layer, growth of the layer will occur at the same time that a portion of the newly grown layer is removed. In this way, the quality of the material grown will be good. Because the growth process and the removal process are independently controllable, the rates of each process can be made equal at any thickness.

For the specific case of an oxide reactive layer, a low power RF oxygen discharge can be used to form the reactive layer. The underlying substrate is fixed to the cathode in the discharge and is both oxidized and sputtered. In this case the growth process is oxidation while the removal process is sputtering. If the oxidizing rate is initially larger than the sputtering rate, an oxide film will form. The oxidizing rate decreases as the oxide thickness increases because oxidation is intrinsically a diffusion-limited process. However, the oxide sputtering rate is independent of the thickness of the bombarded oxide. Therefore, if the oxidation rate is initially higher than the sputtering rate, the oxide thickness will increase until the rate of oxidation becomes equal to the rate of sputtering, at which time a steady state oxide thickness is obtained. This thickness will remain constant independent of time even if the method is continued.

Conversely, if an oxide film is initially present and the sputtering rate is initially larger than the oxidation rate, the oxide thickness will decrease until the oxidation rate and the sputtering rate become equal, at which time a steady-state equilibrium will be achieved. With an applied RF voltage, substantial equality of rates means that over a full cycle of applied RF voltage the oxidation and sputtering cancel one another. It should be understood that within each half cycle of applied RF power, either oxidation or sputtering may dominate; however, after a full cycle, the amount grown is the same as the amount removed. Using this method, very small oxide layers 20–50A in thickness have been formed. Of course, the final thickness of the film can be adjusted by appropriately varying the system parameters. These parameters include the oxygen pressure, the RF power, the composition of the discharge, and the substrate temperature. The rate of sputtering and the rate of oxidation are independently controllable using these parameters; therefore, any desired final thickness can be achieved.

FIG. 1 shows an apparatus used for oxidation and sputtering to form reactive layers. This conventional aputtering apparatus comprises a glass chamber **10** having metal top and bottom plates **11A** and **11B**. RF cathode **12** is held by collar **13** which insulates it from

top plate 11A. Cathode 12 is water-cooled, having an inlet pipe 14 and an outlet pipe 16. The cathode is connected to an RF voltage source which provides an RF discharge at a power density of 0.03 to 2 watts/cm^2.

The cathode is surrounded by a grounded shield 18 which protects against unwanted bombardment of the cathode. The substrates 19, onto which the reactive layer is to be formed, are placed in a substrate holder 20 which is fastened to the cathode 12 by set screws 22. In a typical case, the cathode is copper and the substrate holder is aluminum, although other materials are often used.

Top and bottom metal plates 11A, 11B are grounded and serve as the anode. Connected into the chamber 10 by a valve 24 is a vacuum system comprising a freon-trapped oil defusion pump 25 for providing the desired vacuum. Also connected into the system is a manually controlled leak valve 26 for introduction of the reactive gas species. Valve 26 is connected to a source 27 of reactive gas species (and other gases) and the amount of any gas introduced into chamber 10 is monitored. If desired, the cathode can be surrounded by an aluminum ring which is used for cleaning during an initial DC discharge.

Also included in chamber 10 is a source 28 of material which can be deposited onto substrates 19, or onto formed reactive layers. Insulating material 30 provides electrical isolation from base plate 11B. Located above source 28 is a movable shutter 32 connected to a turning knob 34. Shutter 32 prevents sputtering from source 28 when located above source 28.

The apparatus described is a conventional RF sputtering apparatus; however, the substrates are placed on the cathode rather than being located between the cathode and the anode somewhere in the discharge. In a typical operation, the substrates are initially cleaned by sputter-etching, for instance at a power density of 0.8 watts/cm^2 at an argon pressure of 4×10^{-3} Torr. The argon leak into chamber 10 is balanced by the throttled diffusion pump 25 in order to maintain constant pressure. Typical cleaning times used to remove any residue oxides, photoresistive particles, or other contaminants vary from approximately 1–5 minutes.

Immediately after the sputter-etching cleaning steps, the argon in chamber 10 is removed and is replaced by oxygen or by an argon-oxygen mixture. The reactive oxide layer is formed on substrate 19 by maintaining an RF discharge at a power density of approximately 0.03–0.1 watts/cm^2 for 10 to 20 minutes. In this particular example, a reactive oxide layer having a thickness less than 50A is produced.

The argon in the gas mixture during formation of the reactive layer is ionized and bombards the cathode sputtering away portions of the oxide formed there by the oxygen gas species present in the chamber. If no argon is present, the oxygen gas species themselves will perform the sputtering function, but the sputtering rate will be less than that which occurs when argon is also present in the discharge.

In order to account for the oxide growth, consideration must be given to the sputtering and oxidation processes which occur at the cathode. Most likely, the sputtering occurs in the usual manner as a result of positive ion bombardment while the oxidation is thought to be dependent on the presence of negative oxygen ions. The oxygen discharge is sustained by driving the cathode at a frequency of 13.56 MHz. This results in the usual ion sheath that is visible as a dark space near the cathode surface. The cathode surface potential varies with time having a peak negative value nearly as large as the peak amplitude of the applied potential. Sputtering occurs when positive ions from the sheath are drawn toward the cathode by the negative potential. It is likely that the negative ions for oxide growth are extracted from the plasma or created at the oxide-gas interface by electron attachment. The negative bias resulting from the electron accumulation at the oxide-gas interface may enhance oxidation by providing an additional driving force for diffusion of cations through the oxide. In addition, high energy neutrals and implanted oxygen ions may be important in the sputtering and oxidation processes.

Although the sputtering and oxidation mechanisms have not been identified in detail, insight can be obtained regarding the dependence of oxide thickness on process parameters by assuming that the sputtering and oxidation rates are additive. Accordingly, the rate of oxide thickness change is

$$dx/dt = dx/dt \text{ oxidation} - dx/dt \text{ sputter} \qquad (1)$$

where x is the oxide thickness.

In thermal oxidation, the oxidation rate is generally found to be a decreasing function of oxide thickness. For very thin oxide films, a direct logarithmic growth with time is frequently found. Miles and Smith (referenced previously) have reported a logarithmic oxide growth with time on vacuum deposited Al films exposed (without any external applied potential) to a dc oxygen glow discharge. If, in the present process, the oxidation is assumed to follow a logarithmic law, the oxidation rate may be represented by the expression $Ke^{-x/x}$, where K and x_o are oxidation parameters which depend on factors such as pressure and temperature. In addition, if the sputtering rate is assumed to be a constant (R) when an oxide is present, the Eq. (1) reduces to

$$dx/dt = Ke^{-x/x} - R \text{ for } x > 0 \qquad (2)$$

It is interesting to note from Eq. (2), that a balance between the sputtering and oxidation will occur when $dx/dt = 0$, implying steady state type of saturation in contrast to thermal or dc glow discharge oxidation. The associated steady-state oxide thickness is

$$x_L = x_o \ln (K/R), \qquad (3)$$

hereafter referred to as the limiting oxide thickness. From Eq. (3) it follows that it should be possible to obtain different limiting oxide thicknesses by varying the oxidation and sputtering parameters, e.g., oxygen pressure, RF input power and substrate temperature.

This is consistent with laboratory development in which the limiting oxide thickness was found to increase with oxygen pressure, indicating that the oxidation rate increases more rapidly with oxygen pressure than does the sputtering rate. The oxide thickness could be further adjusted by using an oxygen-argon gas mixture which increased the sputtering rate and decreased the oxidation rate as compared to 100 percent

oxygen. The sputtering rate increases with RF power due to an increase in the ion density and ion energy. Laboratory results indicate that the sputtering rate has a stronger dependence than the oxidation rate on the RF power. Since the energy of the bombarding ions is large compared to kT (k is the Boltzman constant, and T is substrate temperature) little change in sputtering rate occurs for increasing target temperature. However, the oxidation is a diffusion dependent process and is temperature dependent.

If Eq. (2) is integrated, the dependence of oxide thickness of time is obtained, namely,

$$x = x_o \ln [K/R - (K/R - e^{x_i/x_o}) e^{-Rt/x_o}] \text{ for } x > 0 ,$$

4

where x_i is the initial oxide thickness. Eq. (4) reduces to (3) when e^{-Rt/x_o} approaches zero. It should be noted that the limiting oxide thickness might be less than, equal to, or greater than the initial oxide thickness depending on the amplitude of the initial oxidation rate as compared to the sputtering rate.

An effective time constant, $t_o = x_o/R$ can be estimated from Eq. (4). From thermal oxidation data and from oxidation in a dc oxygen glow discharge, x_o is estimated to be in the range of 1.5 to 3.5A. The sputtering rate is about 0.1A/sec for a power density of 0.1 watts/cm^2 for oxygen pressures in the 10^{-2} Torr. range. Hence, the effective time constant is estimated to be about a minute.

The system parameters which can be varied to affect the sputtering/oxidation processes are (1) substrate temperature, (2) RF power, (3) reactive gas species, (4) composition of the gaseous discharge.

If the substrate temperature is varied, the oxidation rate is changed although the sputtering rate is not appreciably affected. Since oxidation is diffusion limited, increasing the substrate temperature will increase the oxidation rate. As the temperature decreases, the oxidation rate will also decrease.

Sputtering rate is dependent on RF power. As the voltage on the cathode increases, there will be a high efficiency of ionization of oxygen and the sputtering rate will increase. While variation of the RF power may also vary oxidation rate, the primary change is to the sputtering rate. Since the voltage on the cathode determines the ion energy striking the cathode, this is a direct way to increase sputtering.

The reactive gas pressure in the discharge (assume that it is oxygen) directly affects the growth process. As the pressure of oxygen in the discharge increases, more oxygen ions will be produced per unit time so the oxidation rate will increase at a constant RF power. However, it is possible that sputtering will increase also since more oxygen ions are present. It has been found that the thickness of films increases when the reactive gas species pressure increases, which indicates that the oxidation (growth) process is primarily increased by varying the reactive gas species pressure.

Varying the composition of the discharge can vary either the oxidation or the sputtering rates, or both. For instance, if additional oxygen is added to the discharge, the oxidation rate will increase. Conversely, if argon is added to the discharge, the sputtering rate will increase.

FIGS. 2A–2C show the growth process, removal process, and the rate of change in these processes. In these figures, it is assumed that the reactive layer to be produced is an oxide layer, although it should be understood that other reactive layers can also be produced by corresponding processes.

In FIG. 2A, the thickness of a reactive layer in the presence of an oxidation process is plotted against time. It is seen that a terminal thickness is eventually achieved, since oxidation is primarily a diffusion limited process.

In FIG. 2B, the thickness of a reactive film removed by a sputtering process is plotted against time. Since sputtering removes the atoms from the reactive layer linearly with time, the plot is a linearly decreasing curve.

FIG. 2C shows a plot of the growth process rate and the removal process rate, for the growth process of FIG. 2A and the removal process of FIG. 2B. The oxidation rate curve decreases exponentially with time, resulting in a substantially constant rate after a sufficient amount of time has passed. The sputtering rate is constant since the curve of the sputtering process (FIG. 2B) is linear. At a time T_0, the oxidation rate and the sputtering rate are equal. At this time, the reactive layer has achieved its final thickness and from then on will maintain this thickness independent of time. This cross-over point of the growth and removal rate curves is determined by the desired final thickness. A particular amount of time T_0 will be required to get to this cross-over point, but from then on the reactive layer will maintain a constant thickness with time. During the applied RF voltage cycle, growth of the reactive layer will predominate during one-half of each cycle, while sputtering (removal) will predominate during the other one-half cycle. Consequently, the average change over a cycle is zero.

FIGS. 3A–3C demonstrate the production of a reactive layer by this process. In FIG. 3A, a substrate having height h is shown at time T_1. This substrate is placed in the apparatus of FIG. 1, and the method as described occurs. Assuming that the reactive layer is to be an oxide, an oxide having a terminal thickness X_L is produced after a time period (T_2-T_1) at the end of which the oxidation rate is equal to the sputtering rate. The new thickness of the oxide/substrate is now ($h+\Delta$), due to expansion when the substrate is oxidized.

At a later time T_3, the oxide has the same final thickness X_L, but the overall thickness of the oxide and the underlying substrate is reduced to a value less than h. As the process continues from time T_2, additional oxide and substrate atoms are sputtered away although the oxide thickness remains constant, since the oxidation rate and the sputtering rate are equal, and remain constant in magnitude.

FIGS. 4A–4C show the effect of a reduction process in accordance with the method of the present invention. In this process, an initial oxide layer exists at time T_1, as shown in FIG. 4A. It is desired to reduce a portion of this oxide layer to leave a layer of pure constituents of the oxide. In FIG. 4B, this is shown as a metal for illustration purposes. For instance, the oxide of FIG. 4A can be lead oxide which is to be reduced into an oxide layer and a pure lead layer.

If the oxide layer of FIG. 4A is a substrate in the apparatus of FIG. 1, and if the reactive gas is hydrogen, the incidence of hydrogen ions on the substrate oxide will reduce the oxide, leaving a pure lead layer on the lead oxide. Again, the rate of hydrogen deposition and

the rate of sputtering from the oxide surface is balanced to produce a pure metal layer of predetermined thickness which remains constant with time, after a steady state equilibrium has been reached at time T_2.

In FIG. 4C, the reduction process has continued, but the thickness of the metal layer remains X_L, since the growth and removal processes are equal, and have constant magnitudes. However, the thickness of the oxide-metal combination is less than *h*.

In the described method, the substrate can be any material including metals and semiconductors. The reactive layers can also be a variety of materials including oxides, nitrides, sulfides, and semiconductors, etc. For instance, if the reactive gas species is H_2S and lead is the substrate, a lead sulfide layer of controlled thickness will be formed. Lead sulfide is a semiconductor material, so this illustrates an example of the production of a controlled thickness of a semiconductor material.

The method is particularly useful in semiconductor technology and in the fabrication of Josephson junction devices. Josephson devices require very thin tunnel barriers having reproducibly uniform thicknesses, and this process is particularly useful. By proper adjustment of the system parameters, a controlled tunnel barrier of any thickness can be produced. The same system can then be used to deposit a counter electrode merely by introducing a source of material to be deposited on the previously produced tunnel barrier. For example, a lead evaporation source **28** can be incorporated in the chamber **10** of FIG. **1.** The substrate could be niobium 6,000A in thickness deposited by RF sputtering in argon at a pressure of 10^{-2} Torr. and at a rate of approximately 400A/minute onto glass substrates held at 670°K. During deposition, the substrate support is grounded. To fabricate the tunnel barrier, the niobium films are affixed to an RF cathode **12** and the above-described method is undertaken to produce an oxide tunnel barrier. The lead counter electrode is then evaporated onto the tunnel barrier.

As stated previously, the operation is not limited to metals or to an oxygen glow discharge. If other gas species or mixtures are used, (for instance H_2, N_2, H_2CH_4, etc.), many other reactive layers can be made. The formation of uniform, dense, short-free, reproducible reactive layers on base materials is achieved in many technologies other than Josephson tunneling devices. For example, semiconductor technology, MOS, and FET structures utilize reactive layers.

Controlled multilayer materials are also obtained by this process, since a reactive gas species can be altered as the depositions proceed. In addition, compositional or different structural forms of various reactive layers can be controlled by varying the reactive conditions, such as temperature, pressure, gas species, ion energy, etc.

What has been described is an improved process for forming reactive layers in which a growth process and a removal process occur simultaneously to offset one another. The rates for each of these processes are independently adjustable and a steady-state equilibrium in which the rates are equal determines the final thickness. In a particular embodiment, oxidation and RF sputtering provide a particularly good working example. However, it should be understood that the principle of this invention includes methods where the growth process is not oxidation and the removal process is not sputtering, as was explained previously.

Films of any kind can be made through the use of competing growth and removal processes to provide films of reproducible final thickness. The film material is deposited on a substrate by any known process (such as evaporation, sputtering, plating, etc.) and a portion of the deposited film is removed simultaneously by any suitable process (such as ion beam, electron beam, sputtering, etc.). The final thickness of the film will be determined by conditions at which the rate of deposition is equal to the rate of removal. When the rates are held equal, the film thickness will remain the same, even if further deposition and removal occurs. Thus the dependence of film thickness on time, which is present when only deposition is used to grow a film, is eliminated as a variable in this process.

What is claimed is:

1. A method for forming reactive layers of controlled thickness on base materials, said reactive layers being combinations of the base material and at least one constituent which reacts with said base material, comprising:

bringing said reactive constituent to said base material in a substantially vacuum environment for reaction thereon to grow said reactive layer at a first rate;

removing said reactive layer simultaneously with said growth, the removal of said reactive layer occurring at a seond rate;

adjusting said first and second rates to be equal for a desired final thickness of said reactive layer;

continuing said growth and said removal at least until said first and second rates of growth and removal respectively are equal, at which time a final thickness of said reactive layer is achieved.

2. The method of claim **1,** where said base material is a metal, and said reactive constituent is oxygen.

3. The method of claim **1,** where said base material is selected from the group consisting essentially of metals and semiconductors, and said reactive constituents are selected from the group consisting of oxygen, nitrogen, hydrogen, sulfur, H_2S , and CH_4.

4. The method of claim **1,** where said first rate is dependent on the thickness of said grown reactive layer and said second rate is substantially independent of the thickness of said reactive layer, said first and seond rates tending to equalize as the thickness of said reactive layer changes.

5. The method of claim **1,** wherein said reactive layer is initially present on said base material, and said second rate is initially greater than said first rate, said rates then varying relatively until a final thickness of said reactive layer is reached at which said first and second rates are equal.

6. The method of claim **1,** where said reactive layer grows by a vapor deposition process.

7. A method of forming reactive layers on base material, said layers having a thickness independent of time after a final thickness is achieved, said method comprising:

placing said base material in a system having a cathode and an anode located in a chamber in which a vacuum can be established, said base material having the electrical potential of said cathode;

introducing a reactive gas species into said chamber, said species being combined with said base mate-

rial to grow said reactive layer thereon when a voltage is established between said cathode and said anode to provide a gaseous plasma between said cathode and said anode, said reactive layer being removed by the incidence of gaseous particles from said plasma as said growth occurs;

adjusting the rate of growth of said layer and the rate of removal of said layer to establish a steady state equilibrium at which said rates are substantially equal, at the final desired thickness of said reactive layer.

8. The method of claim **7,** where said base material is selected from the group consisting of metals and semiconductors, and said reactive species is selected from the group consisting of oxygen, nitrogen, hydrogen, sulfur, CH_4, H_2S, and combinations thereof.

9. The method of claim **7,** where said base material is a metal and said reactive species is oxygen.

10. The method of claim **7,** where a plurality of reactive species are introduced into said chamber, thereby resulting in a reactive layer of variable composition.

11. The method of claim **7,** where an inert gas is also present in said gaseous plasma.

12. The method of claim **7,** where said voltage is an RF voltage applied between said cathode and said anode.

13. A method of producing films of controllable thickness on a substrate, comprising the steps of:

depositing gaseous particles of film material on said substrate, said deposition occurring at a first rate;

removing said film material from said substrate during said deposition, said removal occurring at a second rate which is independently adjustable with respect to said first rate;

adjusting said first and second rates to provide steady state equilibrium conditions at which said rates will be equal;

continuing said deposition and said removal at least until steady state equilibrium is attained.

14. The method of claim **13,** wherein said first rate is dependent on the thickness of said deposited material.

15. The method of claim **13,** including the further step of depositing a layer onto said film material after said steady state equilibrium is attained.

16. The method of claim **13,** where said steady state equilibrium is attained at a film thickness less than about 100A.

17. The method of claim **13,** where said removal occurs by a vapor process.

18. A method of forming reactive layers on substrates, comprising the steps of:

placing said substrate in a vacuum environment housing a cathode and an anode, said substrate being located on the surface of said cathode;

introducing a gaseous ambient between said cathode and said anode, said ambient containing a species which reacts with said substrate to form reactive layers thereon;

establishing a voltage between said cathode and said anode to create an energetic plasma about said substrate whereby said species from said plasma strikes said substrate to form a reactive layer thereon having a first growth rate, said reactive layer also being removed at a second rate by the incidence of particles from said plasma, the growth rate and the removal rate varying relatively to one another as the thickness of said reactive layer changes;

adjusting said first and second rates to be equal at a desired final thickness of said reactive layer;

continuing said growth and said removal at least until said first rate is substantially equal to said second rate.

19. The method of claim **18,** where said reactive layer formation occurs by oxidation and the removal of said reactive layer occurs by sputtering.

20. The method of claim **18,** where said substrate is selected from the group consisting of metals and semiconductors, and said ambient includes a plurality of gaseous species, at least one of said species reacting with said substrate to form said reactive layer.

21. The method of claim **18,** where said gaseous ambient contains at least one gaseous species selected from the group consisting of oxygen, nitrogen, sulfur, hydrogen, CH_4, and H_2S.

22. A method of forming a multi-layer structure comprising the steps of:

placing a substrate in a vacuum environment containing a cathode and an anode, and a source of a first material;

coating said substrate with said first material to form a base layer;

introducing a gaseous ambient between said cathode and said anode, said ambient containing gaseous species which react with said base layer to form a reactive layer thereon;

producing an energetic plasma about said base layer by applying a voltage between said cathode and said anode, said base layer being at said cathode potential, said gaseous species in said plasma striking said base layer and forming a reactive layer on said base layer at a first rate of formation, said reactive layer being removed by the incidence of particles from said plasma, said removal occurring as said reactive layer is being formed and at a second rate of removal;

adjusting the relative rates of formation and removal to provide a steady state equilibrium at which said formation rate will be substantially equal to said removal rate;

continuing said formation and said removal at least until said steady state equilibrium is achieved, at which time said reactive layer will have a desired final thickness;

coating said reactive layer with an electrically conductive material to form a counter layer thereon.

23. The method of claim **22,** wherein said base layer and said counter layer are metals and said reactive layer is an oxide.

24. The method of claim **22,** wherein said voltage is an RF potential and said substrate and base layer are located on said cathode.

25. The method of claim **22,** where said reactive gas species includes at least one of the group consisting of oxygen, nitrogen, hydrogen, sulfur, CH_4, and H_2S.

26. A method for forming reactive layers of controlled thickness on base materials, said reactive layers being combinations of the base material and at least one constituent which reacts with said base material, comprising:

bringing said reactive constituent to said base material for reaction thereon to grow said reactive layer at a first rate;

removing said reactive layer by a sputtering process which occurs simultaneously with said growth, the removal of said reactive layer occurring at a second rate;

adjusting said first and second rates to be equal for a desired final thickness of said reactive layer;

continuing said growth and said removal at least until said first and second rates of growth and removal respectively are equal, at which time a final thickness of said reactive layer is achieved.

27. A method of producing films of controllable thickness on a substrate, comprising the steps of:

depositing particles of film material by oxidation on said substrate, said deposition occurring at a first rate;

removing said film material from said substrate by sputtering during said deposition, said removal occurring at a second rate which is independently adjustable with respect to said first rate;

adjusting said first and second rates to provide steady state equilibrium conditions at which said rates will be equal;

continuing said deposition and said removal at least until said steady state equilibrium is attained.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,849,276

DATED : Nov. 19, 1974

INVENTOR(S) : James H. Greiner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 32, "A 1" should read --Aℓ-- (aluminum).

Column 8, line 37, "$Ke^{-x/x}$ " should read --Ke^{-x/x_o}--.

Column 8, equation 2, should read --$dx/dt = Ke^{-x/x_o} - R$ for $x > 0$--.

Column 9, equation 4, should read

--$x = x_o \ln [K/R - (K/R - e^{x_i/x_o}) e^{-Rt/x_o}]$ for $x > 0$--.

Column 9, line 18, "$e^{-Rt/x}$ " should read --e^{-Rt/x_o}--.

Column 9, line 23, "$t_o = xo/R$" should read --$t_o = x_o/R$--.

Column 11, line 44, "H_2, N_2, H_2CH_4," should read --H_2, N_2, H_2S, CH_4,--.

Signed and Sealed this

eleventh Day of *May 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks