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METHOD OF PRODUCING METALLIC AND DIELECTRIC DEPOSITS BY ELECTRO-CHEMICAL MEANS

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This invention relates to a method of producing metallic or dielectric layers, particularly such layers as are used in the manufacture of capacitors and semiconductor devices.

A simplified flow diagram of the process is as follows:

Loading reaction chamber

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Evacuating Chamber

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Introducing gaseous organo-metallic compound

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Producing luminescent discharge thus decomposing gas and causing deposit on base

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Unloading Chamber

Metallic and dielectric layers may be produced by evaporation of a source material in a vacuum. Such a method of production, however, requires a considerable equipment investment to insure excellent high vacuum conditions and to produce the temperatures which are necessary to effect evaporation. The materials used for the evaporative containers in such a method often cause considerable difficulty where high purity is to be maintained.

The production of metallic layers by means of cathode sputtering is also known. Cathode sputtering, however, requires the input of substantial energy to release the metal atoms from the lattice union of the cathode metal. The method is considered uneconomical because the formation of even thin layers requires considerable time expenditure. Dielectric layers may also be produced by the cathode sputtering method, wherein the sputtering is carried out in the presence of a gas which reacts with the sputtered metal so that oxide layers will be formed. The method of forming dielectric layers has the same disadvantages as the method of forming metallic layers.

The thermal decomposition of the vapors of organic compounds are known to cause the formation of layered deposits. For example, it is possible by thermal decomposition to produce metallic layers from organo-metallic compounds, and to produce silica (SiO_2) layers from ethylsilicate. The method calls for considerable investment because of the high temperatures involved. Also, there is a danger of damaging the carrier, or base, on which the evaporation is to be carried out because of the amount of heat employed in the method.

It is therefore an object of this invention to provide a method of producing metallic or dielectric layers on a base, which method is economical, requires a relatively

small investment, and is safe to use with any base. A further object of this invention is to provide a method for preparing plates for the production of high quality capacitors and semi-conductor devices.

To summarize the method of this invention, in one aspect it consists in the production of metallic or dielectric layers from the vapors of organo-metallic compounds by the action of an ionizing potential under reduced pressure producing a glow discharge. In another aspect it consists in the production of successive layers of metals and dielectrics alternately. Other aspects of the invention consist first in the method of decomposing gases, thus freeing materials for deposit, by use of conduction currents to produce a glow discharge in a suitable tube, and second, in the use of high frequency irradiation of the discharge device to produce the glow, or corona, discharge.

In the practice of this invention an electron discharge chamber, or tube, is employed as a reaction chamber. The chamber contains a cathode and an anode which are spaced apart within the chamber. The cathode and anode are connected by conductors to a source of electrical energy outside the chamber. The chamber is arranged to be evacuated by any suitable evacuation device, such as a vacuum pump, and is further arranged for the introduction of selected gases thereinto. The chamber is further arranged to provide easy access to its interior for the loading of the bases on which layers are to be deposited.

In the practice of the method of this invention the parts to be coated with a layered deposit are placed within the chamber and electrically connected as an anode. The chamber is evacuated, and an organo-metallic compound is introduced. A potential is applied between the anode and cathode, and results in a low current density flow therebetween which causes a glow, or corona, discharge between the anode and cathode which, in turn, causes the organo-metallic compound to decompose. The exact pressure regulation of the chamber may be effected by observing the glow phenomenon. The boundary between the positive column and the cathode dark space preferably lies approximately centered between the electrodes.

As an alternative, the anode and cathode need not be connected by conductors to an outside source of potential. Rather, the glow discharge may be induced by a high frequency field placed across the chamber. In such cases, where the excitation of the gas to the luminescent state is effected by a high frequency field, layers are produced at a speed comparable to the speed of deposit using conductively connected electrodes. The rate of growth of the deposit in both cases, however, is dependent upon the respective conditions of excitation.

The choice of the organo-metallic gases to be employed determines the production of metalliic or dielectric layers. Where a metallic layer is to be produced, oxygen is excluded from the gas introduced therein. When dielectric layers are to be produced, oxygen is mixed with the vapors of the organo-metallic compound as the vapors are introduced into the chamber. After the organo-metallic compound decomposes to yield a metal, the oxygen then causes the metal to oxidize into a dielectric oxide layer, the properties of which can be selected by introducing the proper organo-metallic compound, into the chamber.

Example No. 1

According to the present invention, a metallic layer may be produced on a selected base by the introduction of the vapor of an oxygen-free organo-metallic compound at pressures of 10^{-1} to 10^{-2} millimeters of mercury (mm. Hg) into a previously evacuated chamber of an electron discharge device. The organo-metallic compound has the general formula R—M, where R is an organic radical, and M is a metal combined therewith. Typical compounds which may be employed are lead tetraethyl $Pb(C_2H_5)_4$ and silicium hexamethyl $(H_3)_3 \cdot Si\text{-}Si \cdot (CH_3)_3$. A glow discharge is stimulated in this atmosphere by the use of two electrodes arranged like a plate capacitor spaced about two centimeters apart. One of the electrodes serves as the anode, and the parts to be coated with the metallic layer are deposited thereon, while the other electrode serves as a cathode. At the pressures stated, a potential of 1200 volts having a current density of 0.5 to 1.0 milliampere per square centimeter (ma./cm.^{2}) of the cathode surface is applied to the electrodes. Under the given conditions, a metallic layer with the thickness of one-tenth micron (0.1μ) is produced within a few minutes.

Example No. 2

According to the present invention, a dielectric layer can be produced on a selected base by simultaneously introducing oxygen and the vapors of a metallic carbonyl compound into the evacuated chamber of a discharge device. The metallic carbonyl compound has the general formula M—C=O, where M is as above, and C=O is a carbonyl radical. Typical compounds which may be employed are iron pentacarbonyl $Fe(CO)_5$ and nickel tetracarbonyl $Ni(Co)_4$. Using the operating conditions of Example 1, the glow discharge effects the decomposition of the metallic carbonyl vapors, and due to the reaction of free metal and oxygen, a layer of the oxide of the carbonyl forming metal is produced on the selected base.

Example No. 3

Under the conditions stated in Example No. 1, layers of silica may be produced on selected bases, such as a metal foil and a glass slide, by introducing the vapors of ethylsilicate $[(C_2H_5)_4SiO_4]$, an oxygen containing organo-metallic compound, into the discharge chamber. Optionally, oxygen may also be added or not at the same time. A glow discharge is produced by electrical excitation of the gases and results in the decomposition of the ethylsilicate and in glass-clear layers being produced on the base, which layers predominantly consist of silica (SiO_2). In the practice of the embodiment of this example, it is found that the excitation of the glow discharge by high frequency irradiation leads to layers with better dielectric properties than when the excitation is produced by a potential created across the anode and cathode by conductors connected between them and an outside source of electrical energy.

In all of the above examples, it was found that the thickness of the layers produced by constant pressure and constant discharge current grows linearly with time, and grows more quickly than by use of the conventional methods. The layered deposits produced, in accordance with the inventive method disclosed herein, are of particular interest in the manufacture of capacitors which consist of an alternative arrangement of metallic and dielectric layers. According to the present invention, it is possible either to deposit a dielectric layer on a metallic base, or to produce a metallic layer on a dielectric base. In practice, the method may also be carried out in such a way that metallic and dielectric layers are produced one at a time in turn or in any other desired sequential order. The control of the production of the metallic or dielectric layer is very simply maintained by controlling the gases introduced into the evacuated chamber. For instance, by either adding or not adding oxygen to the input stream, a layer of dielectric or a layer of metallic deposit may be obtained. By alternately adding the vapors of an organo-metallic compound and oxygen, flushing the chamber, and adding the vapors of organo-metallic compound without oxygen, successive layers of dielectric and metal may be built up.

A further field of practical application of the method of this invention is the manufacture of protective layers on semiconductor devices in which, as is well known, the surface has to be protected and stabilized against external influences.

While I have described the principles of my invention in relation to specific embodiments thereof, it should be readily apparent that many variations may be made without departing from the teaching thereof. Accordingly, while I have described my invention with reference to specific embodiments, it is to be understood that the invention is to be interpreted by the state of the prior art and the appended claims.

I claim:

1. A method of depositing a dielectric layer upon a base comprising the steps of loading the base upon which the deposit is to be made into a chamber having a cathode, said base being electrically connected to form an anode, evacuating said chamber, introducting a mixture of a gaseous organo-metallic compound and oxygen into said chamber, said organo-metallic compound having the general formula M—R, where R is an organic radical and M is a metal combined therwith, applying a potential across said anode and said cathode to cause said compound to dissociate and free metal which reacts with the oxygen, and coats said anode with a dielectric layer of metallic oxide.

2. A method as in claim 1 wherein said organo-metallic compound contains a carbonyl group and has the general formula M—C=O where M is a metal and C=O is a carbonyl group.

3. A method of depositing a dielectric material onto a base comprising the steps of loading said base to be coated into a chamber having a cathode disposed therein, said base being electrically connected to form an anode, evacuating said chamber, introducing gaseous ethylsilicate into said chamber, irradiating said gas with a high frequency field to cause said gas to luminesce and decompose and deposit a dielectric coating on said base, maintaining said high frequency field for a predetermined period to control the thickness of deposit, and removing said base after coating.

4. A method of producing a capacitor comprising the steps of inserting a base to be coated into a glow discharge device having a cathode, said base being electrically connected to form an anode, evacuating said device to low atmospheric pressure, introducing into said device a gaseous mixture comprising a predetermined ratio of oxygen and vapors of an organo-metallic compound, exciting said vapors to a glow discharge to produce a dielectric layer on said base, evacuating the residual oxygen and vapors of said organo-metallic compound, introducing into said device an organo-metallic compound in vapor form, exciting a glow discharge in said chamber to form a metallic layer on said dielectric layer, repeating said dielectric layer producing step and said metallic layer producing step until a desired number of layers is built up, returning said device to atmospheric pressure, and applying terminals to the electrodes formed of said metal layers to form a capacitor.

5. A method of depositing alternate layers of metal and dielectric on a base comprising, loading the base to be coated into a chamber having a cathode therein, said base being electrically connected to form an anode, and for depositing the metal layer: evacuating said chamber, introducing a gaseous oxygen-free, organic-metallic compound having the general formula R—M where R is an organic radical and M is a metal combined therewith, applying a potential across said anode and cathode to cause the gaseous organo-metallic compound to glow, maintaining said potential for a predetermined period to dissociate said compound and deposit metal on said anode; and comprising for depositing the dielectric layer, evacuating the chamber, introducing a layer of a gaseous organo-metallic compound and oxygen into said chamber, said

organo-metallic compound having the general formula M—R, where R is an organic radical and M is a metal combined therewith, applying a potential across said anode and said cathode to cause said compound to dissociate and free metal which reacts with the oxygen and coats the anode with a dielectric layer of metallic oxide.

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