

PATENT SPECIFICATION

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(54) METHODS OF AND APPARATUS FOR GENERATING REACTIVE GAS PLASMAS

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED of 195 Broadway, New York City, New York State, United States of America, a Corporation organized and existing under the laws of the State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method and apparatus for generating and maintaining a reactive gas plasma.

Gas plasmas are finding ever-increasing uses. They have been used for some time in cathodic sputtering and related processes for depositing thin films. Exemplary plasma deposition processes are described in British patent No. 1,065,108 and our copending application No. 52475/65 (serial No. 1128603) and application No. 37930/67 (serial No. 1202573) filed concurrently herewith. The effectiveness of high energy plasmas in promoting various chemical reactions at unusually low temperatures has long been recognized. It appears likely that high energy plasma processes will become increasingly important in thin film technology where pyrolytic processes have been dominant. A plasma is defined as a hot ionized gas containing approximately equal numbers of positive and negative ions.

Recent investigations of plasma processes have resulted in a need for a method for establishing a high-energy plasma of highly reactive ion species and sustaining the plasma over long periods for commercial thin film processing. In reactive sputtering processes it is conventional to use a relatively active plasma, usually of oxygen or nitrogen. It is

generally found that after short periods of sputtering the cathode becomes oxidized or passivated and the sputtering rate decreases or sputtering stops completely. The usual method for overcoming this difficulty is to super-impose an RF field on the D.C. discharge field. The RF field continuously depolarizes the cathode and prevents the passivating layer from forming. However, even when this precaution is used the cathode has a limited effective life.

In the above-mentioned application filed concurrently herewith, a process for depositing thin films is described in which the cation of the film deposit is provided by dissociating a compound of the cation in the plasma rather than sputtering it from the cathode. In this case very highly reactive ions are present in the plasma which are capable of corroding or passivating the cathode in a short period of time. The anode is also attacked, although at a slower rate.

According to the invention a method of generating and sustaining a reactive gas plasma for the treatment of an article comprises the steps of producing an electric discharge in a reaction chamber between spaced electrodes, the article being located in the chamber between the electrodes, applying a vacuum pump to an exit port of the chamber, flowing the reactive gas through the chamber, the discharge between the electrodes being such as to ionize the reactive gas and establish the plasma, flowing over at least the electrode most subject to corrosion a gas such as to protect it against corrosion resulting from the reactive plasma and adjusting the flow rates of the reactive gas and the protective gas so that a substantially static interface exists between them.

The presence of the protective gas prevents

the plasma from contacting the electrode and corroding it without interfering with the electrical discharge of electrons or cathode material.

5 Each electrode is conveniently located in a separate chamber connected to the reaction chamber. A gas inlet in each of these chambers then permits the flow of protective gas to envelope the electrode.

10 The invention will now be described in greater detail. In the drawing:

The Figure is a perspective view of the reaction chamber of an apparatus useful according to one embodiment of the invention.

15 The apparatus shown in the Figure consists essentially of a main reaction chamber 10 and two side chambers 11 and 12 for containing the electrodes. The main chamber 20 10 contains a pedestal 13 upon which the substrate 14 is supported. The material from which the pedestal is made is not critical. It is helpful that it be a good heat conductor. Silicon, aluminium, molybdenum, carbon and brass and copper if cooled, are appropriate materials. It is also convenient from the standpoint of avoiding contamination of the substrate that the pedestal and substrate be of the same material. An RF heater 15 is disposed outside the quartz tube inductively coupled with the pedestal for heating the substrate.

25 The chamber 11 contains the anode 16 which is merely a block of a conductive material such as aluminium. The chamber 12 contains the cathode 17 which may be any appropriate electron emitter. It may be an electrode similar to the anode or a thermionic emitter. The cathode composition and structure are not critical.

30 The sole function of the two electrodes in the process and apparatus of this embodiment of the invention is to support the reactive gas plasma. Neither electrode participates in the chemical reaction or directs the flow of free ions. Consequently the two electrodes can advantageously be isolated from the reaction region. This isolation is achieved by creating a protective gas atmosphere around each electrode with the reactive gas plasma confined to the main reaction chamber 10 where deposition is desired. This feature provides some important advantages. Impurities on or in either electrode cannot reach the region of the substrate to contaminate the deposit. More importantly, the electrodes themselves are not consumed, corroded or passivated by direct exposure to the reactive gas plasma.

35 The protective gas for the electrodes is provided, in the apparatus of the Figure, by flowing an appropriate gas such as argon, helium or nitrogen through inlet ports 18 and 19 in the electrode chambers 11 and 12 respectively. Any other inert gases can be used as well. Gases such as carbon dioxide,

air or other gases which are relatively inert to the electrode material can be used as well. It will be appreciated that the presence of an inert gas in the cathode chamber enables the use of a conventional thermionic electron emitter.

The gas reactants for the plasma are admitted through the gas inlet port 20 and are drawn through the reaction chamber by a vacuum source applied to the outlets. The reactants are chosen according to the reaction desired.

The interface between the protective gas enveloping the electrodes and the reactive gas plasma is maintained by balancing the flow rates of the gases against the vacuum pump connected to the common exhaust ports 21 and 22. The boundary of the plasma is easily recognized by visual observation and adjusted by varying the relative flow rates until the interface reaches the desired position namely in the vicinity of the exhaust ports 21 and 22.

The following Example is directed to a specific process for depositing a thin silicon nitride film on a silicon substrate and illustrates one practical use of the method and apparatus for creating a reactive gas plasma.

Example 1

95 The apparatus used was the same as that shown in the Figure. Clean polished silicon slices were placed on a silicon pedestal and sealed into the reaction chamber 10. The pedestal was rotated with a magnetic drive to promote uniformity of the deposit. The substrate was heated to about 350°C. using the RF heater and argon gas was admitted through inlet ports 18 and 19. As an alternative to argon as the protective gas the use of nitrogen is particularly effective. It is also convenient in this particular process since nitrogen is already provided as one of the reactants. A mixture of silicon tetrabromide and nitrogen was admitted through inlet port 20 to give a total pressure of 0.8 torr. The gas pressure determines, in part, the density of the plasma. Pressures which give a useful plasma can be prescribed by the range 0.1 torr to 10 torr. The amount of SiBr₄ was 0.1 per cent by volume of the nitrogen gas. It was found that this parameter could be varied from 0.01 per cent to 1 per cent to give satisfactory results. The plasma was initiated with a Tesla coil between a water-cooled aluminium anode and the cathode at a voltage of 200 volts and a current of 1 ampere. The cathode was a 5U4 electron tube filament drawing 10 amperes at 5 volts. The argon gas flow rate was adjusted until the plasma extended approximately between the two exhaust ports 21 and 22. The short mean free path of the gas molecules at these pressures and the opposing gas flow arrangement prevent the diffusion of the reactive

gases into the anode and cathode compartments.

The silicon substrate was placed so as to be completely immersed in the plasma. An alnico magnet with a field of 2000 to 3000 gauss was mounted on the top of the reaction chamber to deflect the plasma to the region of the substrate. This is an optional expedient which is related to the geometry of the particular apparatus being used. Obviously if the plasma extends unnecessarily beyond the region of the substrate there is a waste of power and gas reactants.

Deposition was continued for 20 minutes after the plasma was struck. A silicon nitride film one half micron in thickness was obtained which showed excellent surface quality and thickness uniformity. The substrate temperature during deposition was 350°C. It was found that good deposits can be obtained over the range of 300°C. to 800°C. Silicon nitride films formed at 300°C. to 400°C. were amorphous which is a desirable characteristic for many applications in semiconductor processing. For instance, amorphous silicon nitride etches more rapidly and uniformly than crystalline films. This property is important where the film is used as a diffusion mask. As the deposition temperature rises above 400°C. the film becomes increasingly crystalline. The substrate derives heat from the plasma during the deposition process. The amount of this heat is determined by the current density of the plasma. Under most conditions prescribed herein it is necessary to supply supplemental heat to the substrate to ensure the proper substrate temperature.

It will be apparent to those skilled in the art that this general method and apparatus for establishing and maintaining a reactive gas plasma will have a variety of useful applications. For instance, in a reactive sputtering process cathode passivation is avoided by flowing a protective gas such as argon, helium or nitrogen around the cathode being sputtered and counter-current to the reactive gas flow so that an equilibrium is established as described above.

The protective gas layer for the anode is less important and in fact is unnecessary in many instances. Where the plasma is used to deposit a film on the anode the protective gas layer will usually be found to be helpful on the cathode only.

By adapting the above plasma technique to

reactive sputtering processes the sputtering rate can be increased considerably, since passivation of the sputtering source is reduced. The sputtered material migrates through the static interface. Silicon sputters more rapidly in argon than in oxygen or nitrogen. Since the rate-determining factor is the rate of ejection of material at the cathode surface, the use of an argon envelope around the cathode increases the rate appreciably.

WHAT WE CLAIM IS:—

1. A method of generating and sustaining a reactive gas plasma for the treatment of an article comprising the steps of producing an electric discharge in a reaction chamber between spaced electrodes, the article being located in the chamber between the electrodes, applying a vacuum pump to an exit port of the chamber, flowing the reactive gas through the chamber, the discharge between the electrodes being such as to ionize the reactive gas and establish the plasma, flowing over at least the electrode most subject to corrosion a gas such as to protect it against corrosion resulting from the reactive plasma and adjusting the flow rates of the reactive gas and the protective gas so that a substantially static interface exists between them.

2. A method according to claim 1 wherein the protective gaseous atmosphere is provided around both electrodes.

3. A method according to claim 1 or 2 wherein the inert gas is argon.

4. A method according to claim 1 or 2 wherein the inert gas is helium or nitrogen.

5. A method according to claim 1 or 2 wherein the protective gas is carbon dioxide or air.

6. A method according to any preceding claim wherein each electrode is located in a separate side chamber connected to the main reaction chamber and a flow of protective gas is produced in each side chamber.

7. A method according to any preceding claim wherein the protective gas is flowed around only the cathode.

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