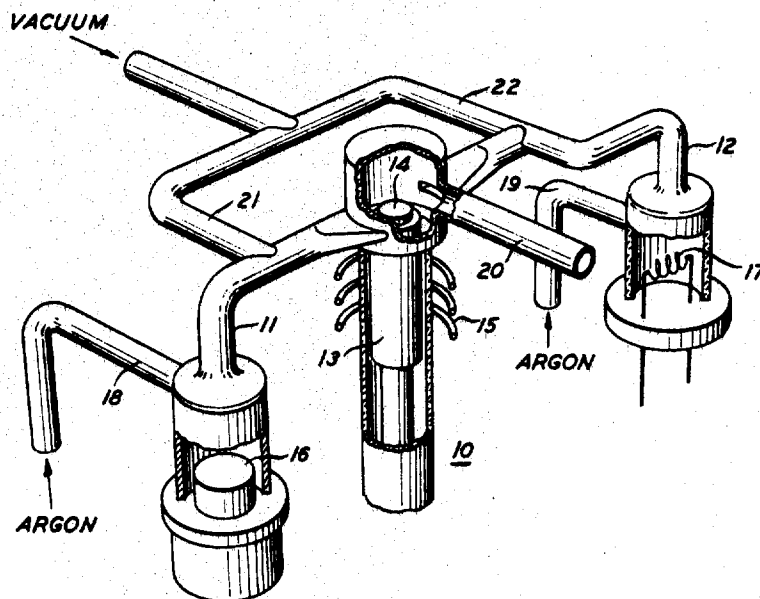


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METHOD AND APPARATUS FOR REACTIVE SPUTTERING WHEREIN THE
SPUTTERING TARGET IS CONTACTED BY AN INERT GAS
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METHOD AND APPARATUS FOR REACTIVE SPUTTERING WHEREIN THE SPUTTERING TARGET IS CONTACTED BY AN INERT GAS

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4 Claims

ABSTRACT OF THE DISCLOSURE

A sputtering target is prevented from passivation during reactive sputtering by maintaining the target in a zone of a discharged supported by an inert gas. The sputtered material migrates through a static interface, to a zone of the discharge supported by a reactive gas, where the sputtered material deposits in compound form on a substrate.

This is a continuation-in-part of our copending application, Ser. No. 579,452, filed Sept. 1, 1966, and now abandoned and 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 and claimed in United States Patent 3,287,243, issued Nov. 22, 1966; and an application being filed concurrently herewith by A. Androshuk, A. A. Bergh and W. C. Erdman, Serial No. 641,094, filed Apr. 28, 1967, and now U.S. Patent 3,424,661. 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.

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 superimpose an RF field on the DC 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 being filed concurrently herewith, a process for depositing thin films is described and claimed 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 this invention the foregoing difficulties are, in whole or part, overcome by continuously flowing a protective gas over the surface of the cathode while

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the plasma reaction proceeds. The anode may be similarly treated. 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.

This aspect of the invention as well as others 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.

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 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, aluminum, 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.

The chamber 11 contains the anode 16 which is merely a block of a conductive material such as aluminum. The chamber 12 contains the cathode 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.

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.

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 of the other inert gases can be used as well. Gases such as carbon dioxide, air or other gases while 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. 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 a 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. It is convenient to operate with the plasma boundary 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 of this invention for creating a reactive gas plasma.

EXAMPLE I

The apparatus used was the same 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 percent by volume of the nitrogen gas. It was found that this parameter could be varied from 0.01 percent to 1 percent to give satisfactory results. The plasma was initiated with a Tesla coil between a water-cooled aluminum 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 here it is necessary to supply supplemental heat to the substrate to insure 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 the plasma deposition process described and claimed in United States Patent 3,287,243 issued Nov. 22, 1966, to J. R. Ligenza, the use of the technique of this invention eliminates the need for an RF field adjacent to the cathode for depassivating the cathode-plasma interface. 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 plasma technique of this invention to reactive sputtering processes the sputtering rate can be increased considerably. 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. Exemplary processes for which the invention can be adapted are described and claimed in United States Patent Nos. 3,073,770 for depositing mullite and 3,242,006 for depositing tantalum nitride.

Various additional modifications and extensions of this invention will become apparent to those skilled in the art. All such variations and deviations which basically rely on the teachings through which this invention has advanced the art are properly considered within the spirit and scope of this invention.

What is claimed is:

1. A method of reactively sputtering comprising the steps of mounting two electrodes including a sputtering target of the material to be sputtered spaced from one another in a vacuum chamber, flowing a protective gas into contact with the surface of at least the sputtering target, the protective gas having a composition which is substantially inert to the sputtering target providing the reactive gas in the space between the electrodes and generating an electric discharge between the two electrodes through the reactive gas while maintaining at least one of the electrodes immersed in the protective gas, and supporting a substrate in the portion of the discharge comprising the reactive gas, whereby particles being sputtered from said target migrate into contact with reactive gas and combine therewith deposit in compound form on said substrate.

2. The method of claim 1 wherein the protective gas is argon, helium or nitrogen.

3. The method of claim 1 wherein both electrodes are maintained in the protective gas.

4. An apparatus for reactively sputtering comprising a closed reaction chamber, vacuum means for establishing a vacuum in said chamber, at least two spaced electrodes in the chamber, including a sputtering target, means for flowing a reactive gas through a portion of the region between the two electrodes, said portion defining a reaction region, means for flowing a protective gas to completely envelop at least said sputtering target, the protective gas having a composition which is relatively inert to the sputtering target the apparatus being adapted so that the flow rate of the reactive gas and the protective gas are such that a static gas interface will exist between the said reaction region and at least sputtering target electrical means for creating an electrical discharge between said electrodes so as to ionize the reactive gas, causing material to be sputtered from said target, and means to support a substrate in said reactive gas, whereby particles being sputtered from said target migrate into contact with said reactive gas and combine therewith to deposit in compound form on said substrate.

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