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(54) **PROTECTIVE COATING ON A SUBSTRATE  
AND METHOD OF MAKING THEREOF**

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(57) **ABSTRACT**

Disclosed herein is a protective coating having a compressive stress of less than 280 Mpa, for devices to be used in a corrosive environment such as halogen containing gases or halogen plasma atmosphere, e.g., wafer supporting device for use in semi-conductor processing assemblies such as electrostatic chucks, heaters, etc. The protective coating in one embodiment is crack-free, with a compressive stress of less than 250 Mpa. It is deposited onto at least one surface of the device via an ion-plating process, in which the Ar flow is kept below 5 sccm, and one embodiment, at 0 sccm, for a crack-free protective layer.

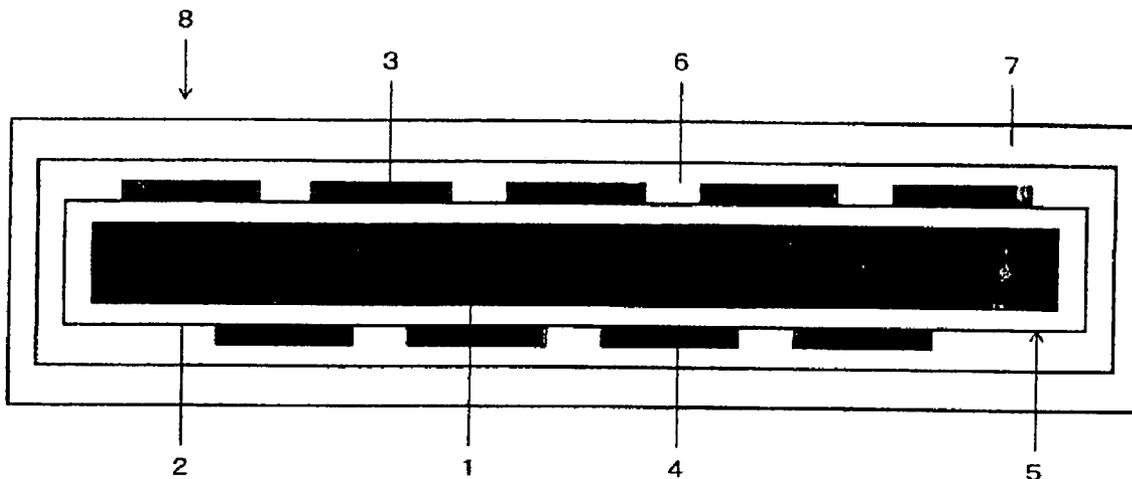
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**Related U.S. Application Data**

(60) Provisional application No. 60/586,059, filed on Jul. 7, 2004.



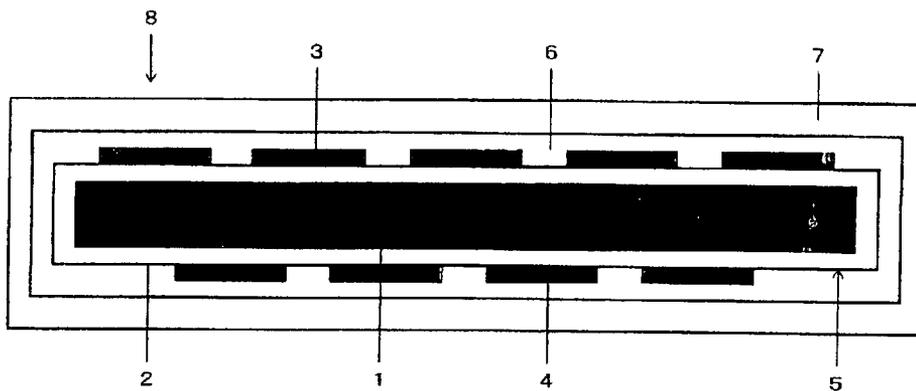


Figure 1



Figure 4

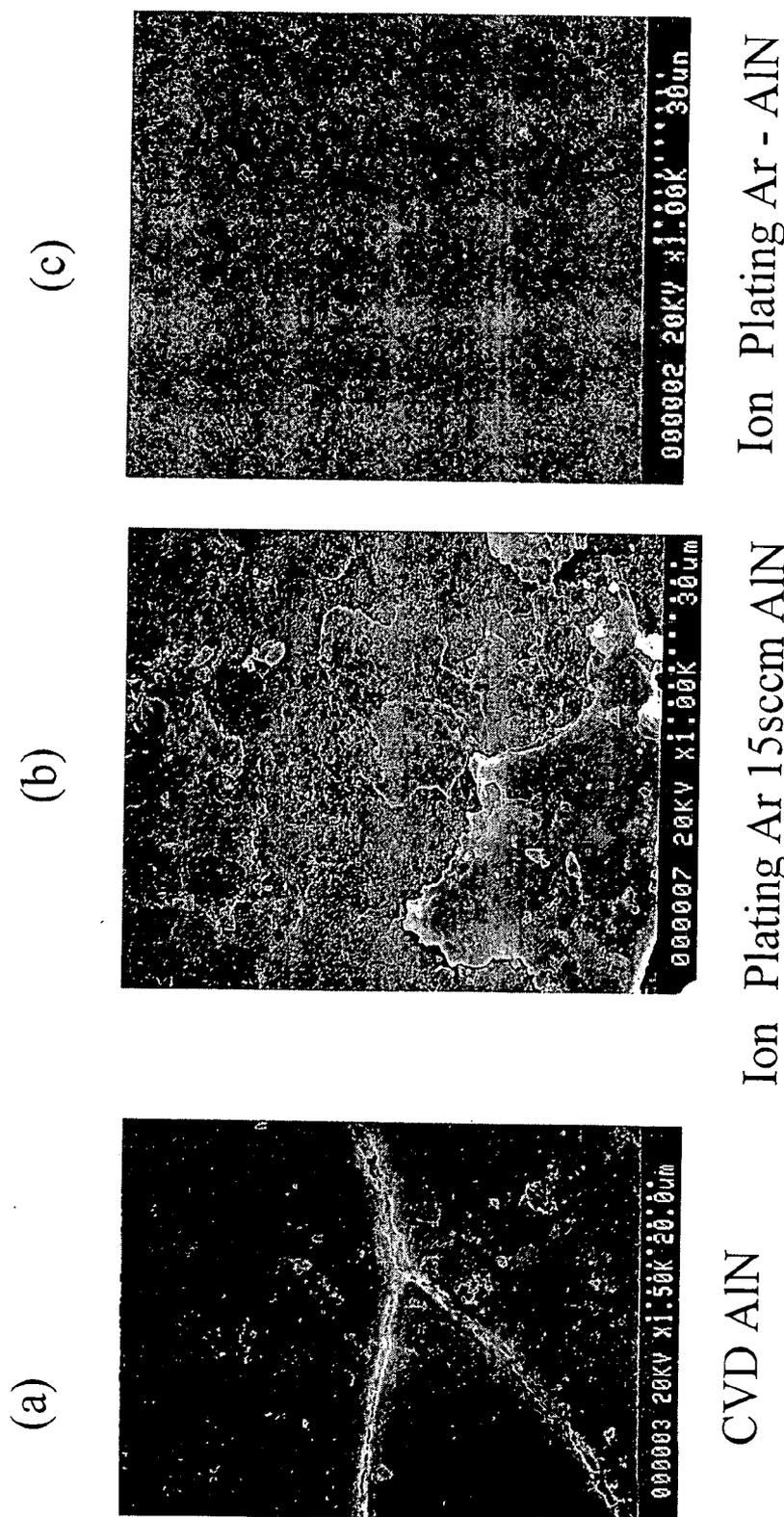
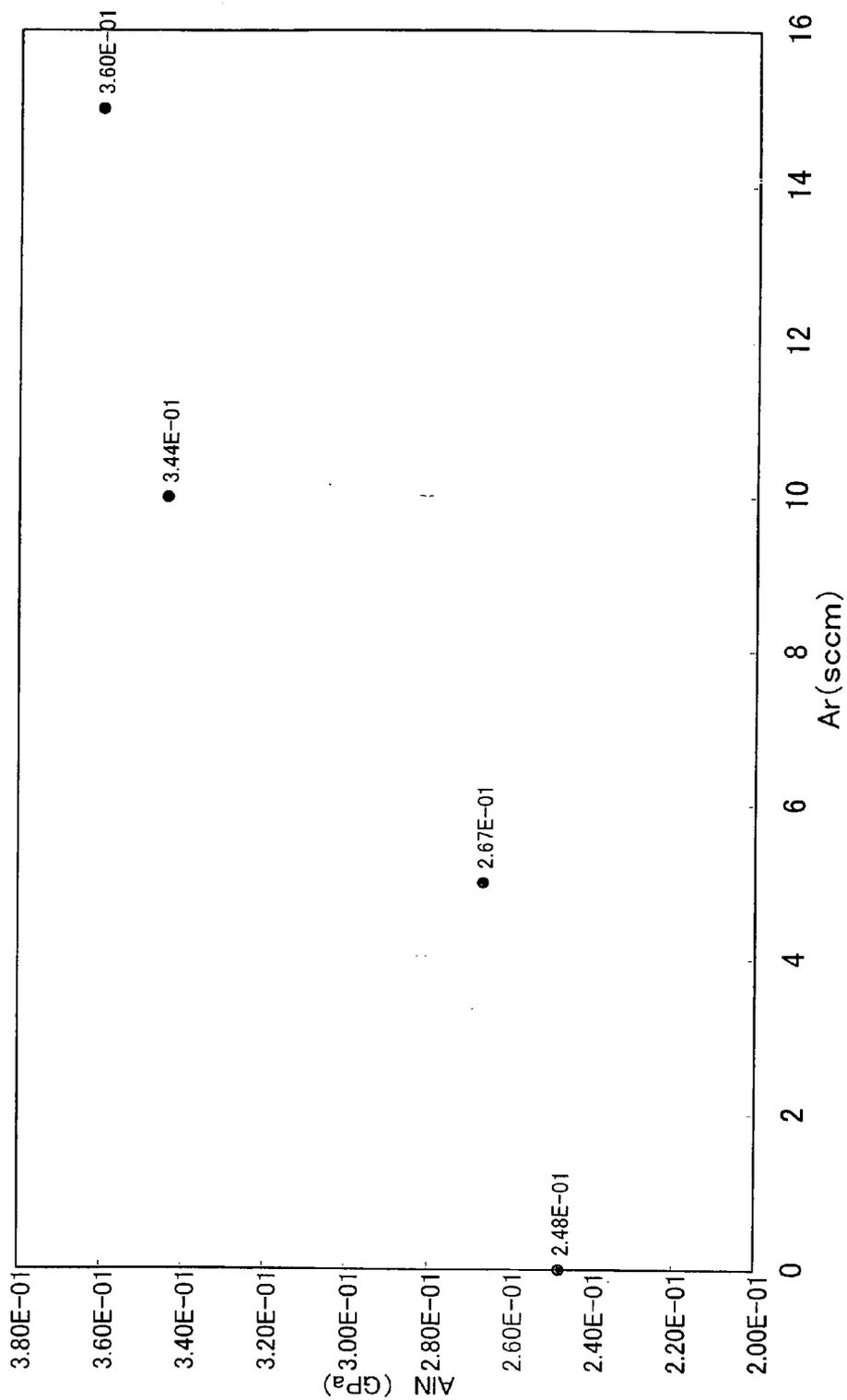


Figure 2

Figure 3



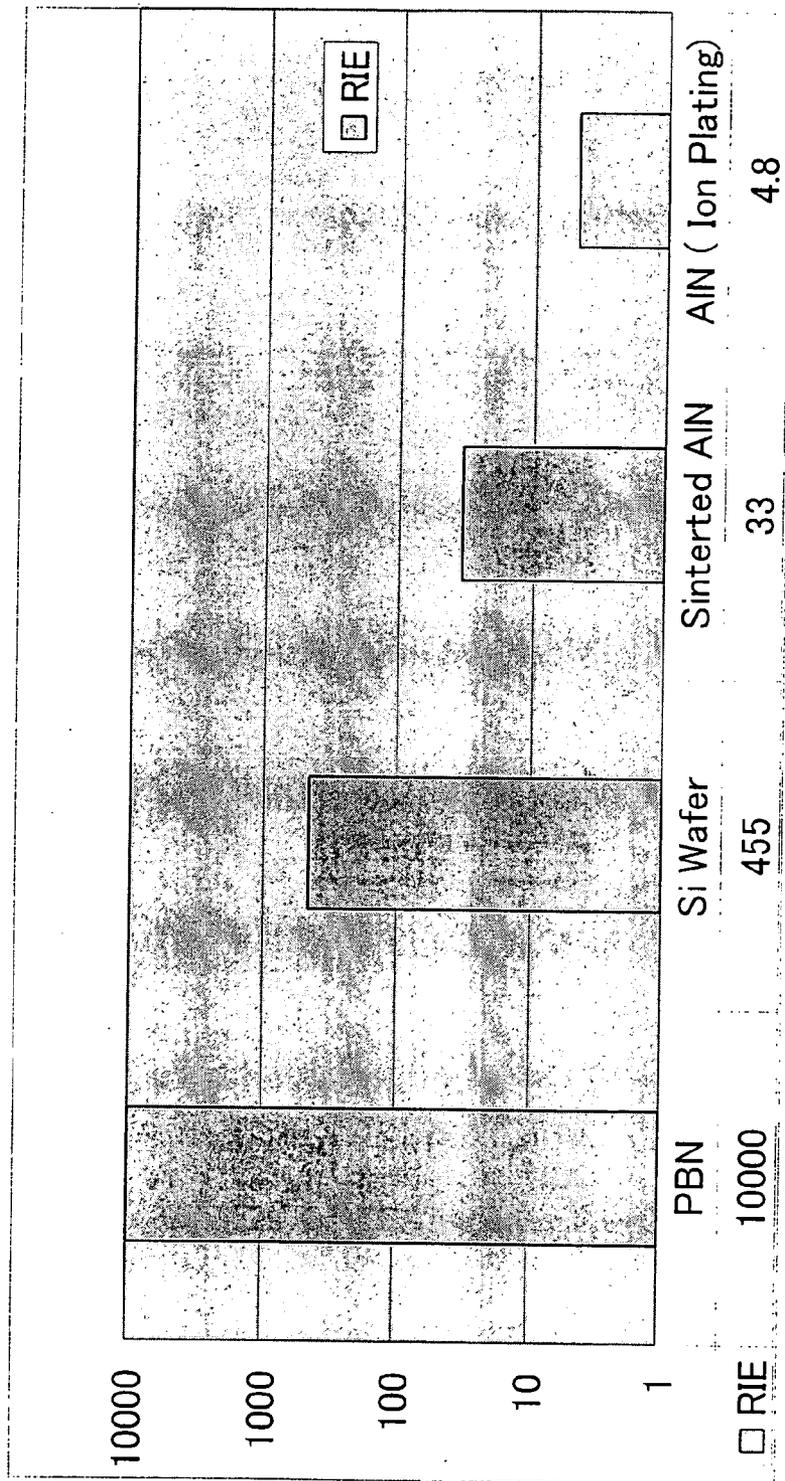


Figure 5

## PROTECTIVE COATING ON A SUBSTRATE AND METHOD OF MAKING THEREOF

### CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 60/586,059, filed Jul. 7, 2004.

### BACKGROUND

[0002] In the semi-conductor industry, equipment is typically exposed to a corrosive environment such as ammonia, hydrogen and halogens at elevated temperatures. Examples of such equipment include substrates, liners, evaporators, crucibles, heating elements, electrostatic chucks, wafer carriers, susceptors, and the like. With respect to the manufacture of computer integrated circuits (e.g., computer chips), a device called electrostatic chuck (ESC) is typically used to support the substrates such as wafer etc., in the process wherein layers of materials are selectively deposited and removed from the wafers.

[0003] During wafer coating, some of the materials that are applied to the wafer or chip also deposit on the equipment in the deposition chamber. This requires periodic cleaning of the equipment, which is commonly done using high-energy gas plasma. Aggressive cleaning agents generally use a halogen-bearing gas such as nitrogen trifluoride ( $\text{NF}_3$ ) to produce fluorine plasma, which cleans the chamber but may simultaneously attack the components of the equipment causing erosion. This erosion limits the life of the components and the equipment. It is therefore desirable to extend the service life of components and equipment by the use of a durable protective coating.

[0004] Japanese Published Patent Application No. JP62-123094A2 discloses susceptors employing a coating layer of AlN formed by a thermal chemical vapor deposition ("CVD") method, on a substrate of high purity carbon based material. Japanese Published Patent Application No. H06-061335 discloses an electrostatic chuck having a protective coating layer comprising AlN,  $\text{Al}_2\text{O}_3$ , AlON, deposited by methods including sputtering, ion plating and CVD methods to protective the underlying PBN layer. PBN does not have anti-corrosive property with respect to halogen gas and halogen plasma. In the protective coating layers of the prior art, there exhibits cracking on the coating thus typically resulting in an etch rate of exceeding 5,000 Angstroms per minute (/min). Peeling is also experienced in the protective coating layers of the prior art.

[0005] Stresses in films are measured using techniques known in the art, e.g., as described in "Mechanical Properties of Thin Films," by W. D. Nix, Metallurgical Transactions A, 20A, 2217 (1989); "The Mechanical Properties of Thin Condensed Films" by R. W. Hoffman, *Physics of Thin Films*, Vol 3, Academic Press, New York, 1966; and P. H. Townsend et al., J. Appl. Phys. 62, 4438 (1987), for multi-layered structures. For AlN coating films, the residual (mechanical) stress is the sum of the stress due to the CTE mismatch between AlN and the substrate, and the intrinsic stress of the AlN as deposited. The total mechanical or residual stress of a film can be summarized by the following formula (1):

$$\text{Stress}(\text{residual})_s = \text{Stress } s_T(\text{thermal}) + \text{Stress } s_i(\text{intrinsic}) \quad (1)$$

[0006] In the equation,  $s_i$  is intrinsic stress, which is a fundamental result of the conditions and method of film growth and is to a large degree a reflection of the film structure and the presence of impurities. The term  $s_T$  refers to the thermal stress in the film due to the CTE mismatch between the film and the substrate. Thermal stress  $s_T$  is dependent on various factors, including the CTE of the substrate, the CTE of the protective film, the processing temperature ( $T_{\text{dep}}$ ) and the reference temperature ( $T_{\text{ref}}$ ), which can be the room temperature or the temperature of the device under operating condition(s) of interest.

[0007] For AlN coatings on pBN substrates, since PBN is a material with low thermal heat expansion coefficient as compared to materials comprising the protective layer such as aluminum nitride, aluminum oxynitride, and the like, etc., there is a strong tensile stress formed in a protective layer that is formed at high temperature and then cooled at room temperature. Because of this reason, cracks and peeling are expected in the protective layer formed in the processes of the prior art.

[0008] There remains a need for protective coating layers of equipment used in corrosive environment, e.g., wafer supporting device such as ESCs, susceptors, heater, etc. to strongly adhere to the underlying substrate. There is also a need for protective coating layers for substrates including pBN, graphite, or combinations thereof, to have excellent anti-corrosion property in halogen gas/halogen plasma environments.

### SUMMARY

[0009] This disclosure relates to a protective coating on a substrate and method of making thereof. In one embodiment, the invention relates to a protective layer for coating at least a surface of a device for use in a halogen-containing gas and/or plasma environment, the protective coating layer having compressive stress of less than 280 Mpa, wherein said surface comprising one of pyrolytic boron nitride, graphite, pyrolytic graphite, and combinations thereof.

[0010] The invention further relates to a protective layer for coating at least a surface of a device for use in a halogen-containing gas and/or plasma environment, wherein the protective coating is under a compressive stress of greater than or equal to about 50 kilograms per square centimeter when disposed upon the substrate, and wherein the coating is deposited on the surface of the device by means of a reactive ion plating method at an Ar flow rate of <6 sccm. In one embodiment of the invention, the Ar flow rate is kept at 0 sccm.

[0011] Lastly, the invention relates to articles comprising the aforementioned protective coating, and articles manufactured by the aforementioned method of making the protective coating.

### BREIF DESCRIPTION OF THE FIGURES

[0012] FIG. 1 illustrates a cross-section view of one embodiment of an article employing the protective coating of this invention, an electrostatic chuck.

[0013] FIG. 2 shows three pictures of AlN coatings. Figure (a) is a scanning electron microscopy (SEM) image showing an AlN protective layer (a) that is formed via a thermal CVD method. Figure (b) is a SEM image showing

an AlN layer (b) that is via an ion-plating method, wherein the Ar flow is kept at about 15 sccm. Figure (c) is a SEM image showing an AlN layer (c) formed via the ion-plating method, with the Ar flow is kept at 05.

[0014] FIG. 3 is a graph illustrating the relationship between the compressive stress of the AlN protective layer and the Ar flow rate in the ion-plating process.

[0015] FIG. 4 contains two diagrams showing the behavior of the protective layer under tensile stress (a) and compressive stress.

[0016] FIG. 5 is a bar chart comparing the etching rates of AlN layer formed via the ion-plating method of one embodiment of the invention, versus protective layers formed by other methods, including pBN and sintered AlN surfaces.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0017] As used herein, the terms “first,” “second,” and the like do not denote any order or importance, but rather are used to distinguish one element from another, and the terms “the,” “a” and “an” do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. Furthermore, all ranges disclosed herein are inclusive of the endpoints and are independently combinable.

[0018] As used herein, approximating language may be applied to modify any quantitative representation that may vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as “about” and “substantially,” may not be limited to the precise value specified, in some cases. In at least some instances, the approximating language may correspond to the precision of an instrument for measuring the value.

[0019] As used herein, “substrate” or “substrates” may be used interchangeably with “surface” or “surfaces.”

[0020] As used herein, “protective coating” layer may be used interchangeably with “coating layer” or “coating film,” or “protective layer,” or “protective coating layer.”

[0021] As used herein, “crack free” or “substantially crack free” means that no cracks can be observed by optical microscopy or SEM with 10 k magnification. Cracks also include holes, perforations, pores, or lines.

[0022] Adhesion means the bonding of two different materials, and cohesion means a mass that resists separation. As used herein, having an excellent adhesion or having a layer that free from peeling, or a coating layer that doesn't peel, means that the adhesive strength of the coating layer exceeds the cohesive strength of underlying layer or layers. The stress at  $T_{ref}$  can be lowered by having  $T_{dep}$  closer to  $T_{ref}$ , or to adjust the intrinsic stress for a given fixed Delta CTE where:

[0023] Stress  $s_T$  (thermal) is proportional to  $((CTE_{sub-strate} - CTE_{film}) * (T_{dep} - T_{ref}))$ .

[0024] As known in the art, the in-film or mechanical stress is a force in the plane of a coating film such as AlN, acting per unit area of the film cross section. The mechanical stress may be compressive or tensile in character. The

compressive stress prevents the formation of cracks thereby increasing the useful life of the article.

[0025] In one embodiment, the invention relates to articles comprising protective coatings that can be advantageously used in harsh semiconductor manufacturing environments that contain ammonia, hydrogen and halogens at elevated temperatures. These coated articles are advantageously used as electrostatic chucks, heater elements and wafer carriers during the manufacture of integrated circuits, semiconductors, silicon wafers, chemical compound semiconductor wafers, liquid crystalline display devices and their glass substrates, or the like.

[0026] Coating Characteristics The protective coating comprises at least one of AlN, AlON, or combinations thereof. In one embodiment, the protective coating layer is a single layer of AlN, AlON, or combinations thereof. In another embodiment, it is a multi-layer of multiple coatings of the same material, e.g., AlN, AlON, etc., or multiple different layers of AlN, AlON, etc., coated in succession.

[0027] In one embodiment, the protective coatings are deposited upon substrates comprising boron nitride (BN), pyrolytic boron nitride (PBN), or carbon doped pyrolytic boron nitride (C-PBN), graphite, pyrolytic graphite (pG), or combinations thereof.

[0028] The protective coatings are also advantageously in a state of compressive stress when disposed upon the substrates, thus facilitating the retention of dimensional stability and mechanical strength as well as a reduction in the number of cracks. The protective coatings also have a substantially reduced number of cracks when compared with other protective coatings manufactured by processes such as thermal chemical vapor deposition. In one embodiment, the protective coating has excellent adhesion to the substrate and is crack free. The reduced number of cracks as well as the morphology of the coating minimizes any etching of the substrate during the periodic cleaning of the equipment.

[0029] When applied to a substrate, the protective coating layer of the invention significantly increases the life cycle of the article. The life cycle is the amount of time that the article can be subjected to a cleansing environment before it has to be replaced as a result of the etching away of the protective coating. Examples of suitable cleansing environments include halogen-based plasmas, halogen-based radicals generated from remote plasma source, halogen-based species decomposed by heating, halogen-based gases, oxygen plasmas, oxygen-based plasmas, or the like. An example of a halogen-based plasma is a nitrogen trifluoride ( $NF_3$ ) plasma. Fluorinated hydrocarbons such as, for example, carbon tetrafluoride ( $CF_4$ ) can be used either alone or in combination with oxygen. The article may also be subjected to a reactive ion-etching environment and should be capable of offering resistance to etching in such an environment as well.

[0030] In one embodiment, the protective coating increases the life cycle of the article by a time period of greater than or equal to about 5 hours over articles that have unprotected PBN as a substrate. In one embodiment, the protective coating increases the life cycle of the article by a time period of greater than or equal to about 10 hours over similar articles that have unprotected PBN. In yet another embodiment, the protective coating increases the life cycle

of the article by a time period of greater than or equal to about 50 hours over similar articles that have unprotected PBN. In yet another embodiment, the protective coating increases the life cycle of the article by a time period of greater than or equal to about 100 hours over similar articles that have unprotected PBN.

[0031] The thickness of the protective coating may be varied depending upon the application and upon the cleaning conditions. Protective coatings having thickness of about 1 to about 5  $\mu\text{m}$ , generally permit good thermal contact between the wafer and the electrostatic chuck, but do not last as long as coatings having greater thicknesses. Coatings having thicknesses of greater than 5  $\mu\text{m}$ , however, have longer life cycles than coatings having thickness of less than 5  $\mu\text{m}$ . In one embodiment, the coating has a thickness of greater than or equal to about 2 micrometers ( $\mu\text{m}$ ). In another embodiment, the protective coating thickness is greater than or equal to about 10  $\mu\text{m}$ . In a third embodiment, the thickness is greater than or equal to about 50  $\mu\text{m}$ . In yet another embodiment, the thickness is greater than or equal to about 75  $\mu\text{m}$ .

[0032] As known in the art, compressive stress in protective coating films or layers prevents the formation of cracks thereby increasing the useful life of the article. The protective coatings of the present invention are generally under compressive stress when deposited upon substrates comprising PBN, PG or C-PBN.

[0033] In one embodiment, the protective film has a compressive stress of less than 300 MPa. In a second embodiment, the film has a compressive stress of less than 280 MPa. In a third embodiment, the film has a compressive stress of less than 250 MPa.

[0034] The compressive stress permits the protective coating to withstand thermal cycling without cracking. The protective coatings have very few cracks and this feature provides significant resistance against etching. In one embodiment, the initial protective coating may have cracks that occupy a volume of less than 10% of the total volume of the coating. In another embodiment, the initial protective coating may have cracks that occupy a volume of less than 5% of the total volume of the coating. In yet another embodiment, the protective coating may be completely crack free when it is initially manufactured.

[0035] The protective coating is characterized as being etch-resistant, or having a low-etch rate in an environment comprising halogens or when exposed to plasma etching, reactive ion etching, plasma cleaning and gas cleaning. The etch rate for the protective coating is much lower than coatings of a similar chemical composition that are sintered. The etch rate of the protective coating is also less than the etch rate for the PBN substrate. This low etch rate provides protection for the PBN thereby extending the life of the article. In one embodiment, the etch rate is less than 100 Angstroms per minute (/min). In a second embodiment, the etch rate is less than 50/min. In a third embodiment; it is less than or equal to about 40 Angstroms per minute (/min) in a cleansing environment that comprises halogens or when exposed to a reactive ion etching environment.

[0036] Process of depositing the protective coating—IP the protective coating is deposited using ion plating (IP). In ion plating, aluminum is ionized using a radio frequency

(RF) discharge. Ionization and plasma is mainly sustained by the formation of nitrogen ions from nitrogen. Ionization is brought by plasma discharge, which can be sustained not only by RF coils but also by using a capacitive coupling plasma or an inductive coupling plasma. The chamber in which the deposition occurs is generally maintained under vacuum conditions. Nitrogen gas is introduced into the chamber and becomes ionized by RF discharge. The substrate is generally placed on or near a cathode to direct the ionized gases. The substrate is placed in an argon/nitrogen plasma, together with the aluminum metal, which vaporizes on heating and becomes partly ionized (acquires charged atoms) as it diffuses through the discharging region to form the protective coating.

[0037] The temperature in the chamber during ion plating is maintained at less than or equal to about 400° C. The deposition rate during ion plating is greater than or equal to about 0.1  $\mu\text{m}/\text{hour}$ . In one embodiment, the deposition rate is greater than or equal to about 0.15  $\mu\text{m}/\text{hour}$ . In another embodiment, the deposition rate is greater than or equal to about 0.20  $\mu\text{m}/\text{hour}$ . In yet another embodiment, the deposition rate is greater than or equal to about 0.25  $\mu\text{m}/\text{hour}$ .

[0038] In an ion plating method, an inert/non-reactive gas such as Argon can be introduced into the vacuum reactor. Applicants have found that by controlling the Ar flow amount in the reactor, the anti-corrosive property of the protective coating layer can be controlled, for an anti-corrosive protective layer with no cracks/minimal or no peeling (strong adhesion strength between the coating layer and the pBN/pG substrate).

[0039] In one embodiment of the ion-plating process, when the Ar flow is reduced to 10 sccm, there is some evidence of peeling along the entire protective layer. When the Ar flow is reduced to 5 sccm, peeling is observed in one some part of the protective layer. In one embodiment wherein the Ar flow is kept below 6 sccm, the protective coating layer displays a compressive stress of less than 280 Mpa and little if no peeling. In another embodiment, the Ar flow rate is kept at 0 sccm for a crack-free protective layer that also adheres to the substrate (without peeling), and with a compressive stress of less than 250 Mpa.

[0040] Applications of the Invention The protective coatings can be advantageously used for semi-conductor processing components such as substrates, liners, evaporators, crucibles, heating elements, wafer carriers, electrostatic chucks, susceptors, or the like. The protective coating enhances the life of the aforementioned semi-conductor processing components when these components are exposed to ammonia, hydrogen, halogens such as fluorine, chlorine, nitrogen trifluoride, or the like, at temperatures of greater than or equal to about 200° C.

[0041] FIG. 1 illustrates the cross section of an article employing the protective coating of the invention. The article can be a heating element, an electrostatic chuck or a wafer carrier that can be used for locating and/or heating the silicon wafers during the deposition of surface layers on the wafer. In one embodiment, the article 8 is an electrostatic chuck. The article comprises a graphite core 1 of about 10 mm. The core can also be made from PBN, hot pressed BN, or composites. Disposed upon the graphite core is a pyrolytic boron nitride (BN) layer 2 of about 300  $\mu\text{m}$ . In one embodiment, the pBN layer 2 is can be deposited by thermal

chemical vapor deposition (thermal CVD), hot pressing, sintering, or plasma enhanced chemical vapor deposition (PECVD).

[0042] Disposed upon the BN layer 2 is a layer of pyrolytic graphite (PG). The PG layer is deposited upon the BN layer 2 by chemical vapor deposition (CVD) or other processes known in the prior art. The PG layer is machined into a desired configuration, forming chuck electrode(s) 3 at the top surface and heater electrode (4) at the bottom surface of the article. The machined PG layer 3 and 4, together with the first pBN layer 2 and the graphite substrate 1, form the substrate body 5 of the article. A pyrolytic boron nitride (PBN) coating 6 is disposed upon the body of the article such that it substantially covers the body of the article. The pBN coating layer 6 is formed in a thermal CVD furnace at 1850° C., under reduced pressure with 3 moles of ammonia and 2.4 moles of methane gas with respect to 1 mole of boron trichloride. A carbon-doped PBN insulation layer 6 of a thickness of 100 about  $\mu\text{m}$  is formed on the entire surface of substrate 5, having an electrical resistivity of  $2.8 \times 10^{12} \Omega\text{-cm}$ .

[0043] This PBN coating 6 resists oxidation, provides electrical insulation, chemical and mechanical protection and minimizes the opportunity for carbon contamination of the wafers. It also has very high thermal conductivity in the a-b direction, thereby minimizing any thermal non-uniformity on the top of the heater. The protective coating AlN 7 is then disposed upon the PBN coating 6.

[0044] In one embodiment to provide the electrostatic chuck protection to be usable even in a corrosive environment such as halogen gases and/or halogen plasma atmosphere, the AlN coating layer 7 is applied onto the electrostatic chuck 8 in a reactive ion plating process, wherein the Ar flow rates are kept at 0 sccm (no Ar), 5 sccm, 10 sccm, and 15 sccm respectively. In the ion plating process, nitrogen reacts with aluminum at about 400° C. forming as the AlN protective layer 7 of the invention with anti-corrosive property with respect to halogen gas and halogen plasma.

[0045] As a comparative example on a comparative electrostatic chuck, instead of using an AlN protective coating via ion-plating method, an AlN protective layer is formed using a thermal CVD method at 950° C. FIGS. 2 (a)-2(c) are SEM (Scanning Electron Microscope) images, comparing the AlN protective layers of the invention with the prior art AlN coating via thermal CVD.

[0046] FIG. 2 (a) shows cracks in the AlN layer formed by a thermal CVD process, confirming that it is not practical to employ this coating in a corrosive environment. FIG. 2 (c) is an SEM showing an AlN coating formed by the ion-plating method, wherein the Ar flow rate is reduced to 0, thus forming a crack-free AlN layer and without forming. FIG. 2 (b) is an SEM showing that when the Ar flow is reduced to 15 sccm, the AlN layer remains crack-free although there is some showing of peeling.

[0047] FIG. 3 is a graph illustrating the relationship between the compressive stress of the AlN protective layer and the Ar flow rate in the ion-plating process. In one embodiment wherein the AlN protective layer 7 thickness of 0.5  $\mu\text{m}$  is formed, with the Young's Modulus value is 130 GPa and the Poisson ratio is measured as 0.28 by the deflection method, the compressive stress is measured to be

248 Mpa when the Ar flow amount is reduced to 0 sccm. The compressive stress is measured to be 267 Mpa when the Ar flow rate is kept at 5 sccm. When the Ar flow is set at 10 sccm, the compressive stress is 344 Mpa. Finally, when the Ar flow rate is 15 sccm, the compressive stress is 360 Mpa. A

[0048] It should be note that the AlN protective layer formed by the thermal CVD method whose SEM is shown in FIG. 2 (a), the compressive stress cannot be measured since all samples show evidence of cracks.

[0049] FIG. 4 contains two diagrams showing the behavior of the protective layer under tensile stress (a) and compressive stress. As illustrated in the prior art AlN coating via thermal CVD and with the occurrence of cracks, the thermal heat expansion coefficient of pBN is small comparing to materials comprising the protective layer such as aluminum nitride, aluminum oxynitride, and the like, etc. Since there is a strong tensile stress due to the difference in thermal expansion coefficients and this residual tensile stress exceeds the tensile strength of the protective layer itself, the protective layer is ruptured thus causing cracks. This is illustrated in FIG. 4 (a). In the AlN protective layer formed via an ion-plating method and as illustrated in FIG. 4 (b), compressive stress is formed and thus minimizing or eliminating the occurrence of cracks.

[0050] FIG. 5 is a graph comparing the anti-corrosion property of the AlN coating layer of the invention as formed via the ion-plating process, with other protective surfaces. The anti-corrosion property is illustrated as the etch rate under a NF3 plasma atmosphere, the lower the rate, the higher the anti-corrosion property. In the Figure, etch rates measured in an AlN protective layer formed by the ion-plating method wherein the Ar flow is 0 sccm is compared with the etch rates as measured in sintered AlN, thermal CVD pBN, and Si wafer. The etch rates of the ion-plated AlN of the present invention is at 4.8 Å/minute, as compared to rates in sintered AlN of 33 Å/min., 455 Å/minute in Si wafer, and >10,000 Å/minute in pBN.

1. A protective layer for coating at least a surface of an article for use in a halogen-containing gas and/or plasma environment,

wherein said at least a surface comprises one of pyrolytic boron nitride, graphite, pyrolytic graphite, and combinations thereof,

wherein the protective layer has a compressive stress of less than 280 Mpa.

2. The protective layer of claim 1, wherein the protective layer has a compressive stress of less than 250 Mpa.

3. The protective layer of claim 1, wherein the protective layer comprises one of aluminum nitride, aluminum oxynitride, and combinations thereof.

4. The protective layer of claim 1, wherein the protective layer is deposited onto said at least a surface of an article via an ion plating method.

5. The protective layer of claim 4, wherein the protective layer is deposited onto said at least a surface of an article via an ion plating method.

6. The protective layer of claim 5, wherein ion plating method includes Argon as a non-reactive gas.

7. The protective layer of claim 6, wherein the Argon flow rate is kept below a rate of 10 sccm.

8. The protective layer of claim 7, wherein the Argon flow rate is kept below a rate of 5 sccm.

9. The protective layer of claim 1, wherein at least a surface comprises pyrolytic boron nitride.

10. The protective layer of claim 1, wherein the protective layer comprises aluminum nitride.

11. The protective layer of claim 1, wherein the protective layer has a thickness in the range between 3 μm to 200 μm.

12. The protective coating layer of claim 1, wherein the protective layer is substantially crack-free.

13. The protective coating layer of claim 1, wherein the layer has an etch resistance rate of less than 50 Angstroms per minute upon exposure to a halogen-containing gas and/or plasma environment.

14. The protective coating layer of claim 13, wherein the layer has an etch resistance rate of less than 40 Angstroms per minute upon exposure to a fluorine-containing gas and/or plasma environment.

15. An article comprising a protective coating layer on at least one of its surfaces, said coating layer comprises at least one of aluminum nitride, aluminum oxynitride or combinations thereof,

and wherein the coating layer is substantially crack free when said article is exposed to fluorine containing gases and/or plasma.

16. The article of claim 13, wherein the protective coating layer has a compressive stress of less than 280 Mpa.

17. A method for modifying the in-film stress in a protective coating layer of an article for use in a halogen-containing gas and/or plasma environment, said method comprising:

depositing a protective coating layer on at least one surface of the article, said coating layer comprising at least one of aluminum nitride, carbon and/or oxygen doped aluminum nitride, aluminum oxynitride or combinations thereof,

said at least one surface comprises at least one of pyrolytic boron nitride, pyrolytic graphite and/or carbon doped boron nitride, and combinations thereof;

wherein said protective coating layer is substantially crack free upon exposure to said halogen-containing gas and/or plasma environment.

18. The method of claim 17, wherein the deposited coating layer has a compressive stress of less than 280 Mpa.

19. The method of claim 17, wherein the protective coating layer is deposited on said at least one surface via an ion plating method.

20. The method of claim 19, wherein the ion plating method includes Ar as a non-reactive gas, and wherein the Ar gas flow rate is maintained at an average of less than 10 sccm.

21. The method of claim 17, wherein the protective coating layer has an adhesion strength which exceeds the cohesive strength of the surface protected by said coating layer.

22. The method of claim 17, wherein said at least one surface of the article is first protected by depositing at least a layer of pyrolytic boron nitride, pyrolytic graphite and/or carbon doped boron nitride on said surface.

23. An article manufactured the method of claim 28.

24. The protective layer of claim 1, wherein the layer is a multilayer.

25. The protective layer of claim 1, wherein the protective coating layer has an adhesion strength which exceeds the cohesive strength of the surface protected by said coating layer.

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