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**METHOD FOR FORMING NOBLE METAL OXIDES
AND STRUCTURES FORMED THEREOF** ✓

Field of the Invention

The present invention generally relates to a method for forming noble metal oxides and structures formed thereof; more particularly, it relates to a method for forming noble metal oxides by exposing a noble metal surface to an oxygen containing plasma energy source or ion beam, thereby forming a surface layer of noble metal oxide such that improved adhesion and interface properties are achieved with a subsequently deposited layer.

Background of the Invention

In the development of ULSI memory devices, and specifically for those memory devices fabricated by sub-half-micron technology, device sizes are continually being reduced in order to minimize the chip real estate used. One of the more recently developed fabrication methods for achieving such a goal in dynamic random access memory (DRAM) devices incorporates building capacitors with a stack capacitor geometry. In a stack capacitor fabricated for a DRAM device, a high-permittivity (or high-epsilon) material is frequently used as the dielectric insulator for the capacitor structure for its desirable high dielectric constant. Similar structures incorporating ferroelectric materials can also be used to form non-volatile memory devices such as NVRAM.

For instance, in recently developed fabrication processes for the DRAM capacitors,

high-epsilon materials such as barium strontium titanate (BST), lead lanthanum titanate (PLT), lead zirconium titanate (PZT), bismuth titanate and other types of perovskite insulator materials have been utilized in such structures.

The use of high-epsilon materials generally requires base electrodes made of noble metals in order to minimize the effect of interfaces of low permittivity capacitance which would otherwise lower the overall capacitance of the structure. Noble metals such as Pt, Ir, Ag, Au, Ru, Pd, Os and Rh are typical candidate electrode materials for memory devices incorporating high-epsilon materials based on their desirable high conductance and their resistance to oxidation during a subsequent deposition process for a dielectric insulator. Of the various noble metal materials, Pt and Ir are good examples for use as noble metal electrodes. However, a problem observed in depositing a perovskite-type insulator material on top of these and other substrates is the difficulty in maintaining the correct oxygen stoichiometry in the perovskite material. Loss of oxygen, from either the bulk of the high permittivity material, or from an interfacial surface layer at the dielectric/electrode interface can result in a number of problems. For example, oxygen-poor phases of these high permittivity materials tend to have lower dielectric constants. In addition, oxygen vacancies in the dielectric can lead to undesirably higher leakage currents, either by making the dielectric more conductive, or by lowering the barrier height for carrier injection from the electrode at the electrode/dielectric interface. Defects due to oxygen vacancies can also oscillate in response to applied fields and contribute to ac losses.

While the excellent oxidation resistance of most noble metal materials is typically

regarded as a desirable characteristic in an electrode, it may be a disadvantage in cases where the presence of a noble metal oxide may be useful in promoting surface adhesion. Surface layers of noble metal oxides are useful in adhesion promotion when preparing oxygen-rich noble metal/dielectric interfaces that are desirable in electronic devices containing high-permittivity materials.

Figure 1 is an illustration of a conventional DRAM capacitor structure which might be incorporated into a semiconductor memory device such as that shown, for example, in Serial No. 08/866,460 (Case Y(996-080) by C. Cabral, Jr. et al and Serial No. 08/886,459 (Case YO996-176) by A. Grill et al, both filed May 30, 1997 and assigned to the IBM Corporation. Capacitor 10 is built on a pre-processed silicon substrate on top of an oxide insulating layer 12 and a silicon contact plug 16. It is constructed by first depositing and then forming a bottom electrode 20 from a noble metal such as Pt, Pd, Ir, Ag, Au, Ru, Pd, Os and Rh. A high dielectric constant material, i.e., a high-epsilon material such as barium strontium titanate or lead lanthanum titanate is then deposited to cover the bottom electrode 20 forming an insulating layer 24. On top of the insulating layer 24, a second electrode layer 28 formed of a similar noble metal material is then deposited for use as a top plate electrode.

The chemical inertness of the noble metal materials may contribute to poor adhesion at noble metal interfaces with other materials. For instance, other than the high-epsilon materials, spin-on-glasses (SOG) supplied as FOx[®] by Dow Corning and as HSG[®] by Hitachi may also be desirable inexpensive insulating dielectric materials for use in structures containing

noble metals, for example, as an insulating isolation layer over plate electrode 28 shown in Figure 1. However, the SOG materials may be difficult to use in such applications due to their poor adhesion.

Others have recognized that the presence of surface contaminants in the form of very thin carbon or oxide layers can affect the diffusion and reaction of atoms deposited on a metal surface. The thin surface films thus formed tend to be detrimental to good adhesion and are therefore, generally eliminated prior to a deposition process. There have been cases where the presence of a surface oxide layer is beneficial. For instance, U.S. Patent 5,382,447 to Kaja et al teaches the use of a Co_3O_4 -like oxide film having a thickness of about 50Å for enhancing the bonding of a spin-on polyimide precursor onto a Co substrate. It was assumed that the surface oxygen bonds in the oxide layer may have a strong chemical interaction with the arriving cations, and thus leading to improved adhesion. There is also an assumption of an electrostatic mechanism of adhesion for non-metallic coatings due to a positive charge transfer occurring across the interface based on a difference in electron affinities and the presence of surface states in the oxide.

Others have attempted to solve the problem of poor adhesion between a spin-on-glass and platinum by using SOG alternatives such as a sputter-deposited quartz material. However, relative to SOG, sputtering is an expensive process to carry out and moreover, is ineffective in filling small gaps. While the gap filling problem may be minimized, by using the sputter-deposited quartz only as a thin adhesion layer (between 100~200 Å) between Pt and SOG,

this comes at the expense of higher cost. Still others have used an evaporated or sputtered adhesion layer such as Ti. Even though a thin Ti layer has proven effective as an adhesion layer, the possible diffusion of Ti from the Pt surface into other regions of the electrode/high-epsilon structure makes the process highly undesirable.

It is therefore an object of the present invention to provide a method for improving the adhesion and interface properties of a noble metal and a subsequently deposited high dielectric constant material that does not have the drawbacks or shortcomings of the conventional deposition methods.

It is another object of the present invention to provide a method for improving the adhesion and interface properties of a noble metal and a subsequently deposited oxide-containing material by first forming a noble metal oxide layer in the top surface of the noble metal substrate.

It is a further object of the present invention to provide a method for improving the adhesion and interface properties of a noble metal and a subsequently deposited high dielectric constant material by exposing the surface of the noble metal to an oxygen-containing plasma or ion beam such that a layer of noble metal oxide is first formed on the noble metal substrate.

It is another further object of the present invention to provide a method for improving the adhesion and interface properties of a high dielectric constant material deposited

on a noble metal by first exposing a surface of the noble metal to an oxygen-containing plasma or ion beam for a sufficient length of time such that a layer of between 0.4 nm and 10 nm of noble metal oxide is formed and sandwiched between the high dielectric constant material and the noble metal.

It is still another object of the present invention to provide a noble metal oxide film by exposing the surface of a noble metal substrate to an oxygen-containing plasma energy source or ion beam.

It is yet another object of the present invention to provide a method for depositing a high-permittivity material onto a noble metal substrate by first exposing a top surface of the noble metal substrate to an oxygen-containing energy source for a sufficient length of time until an adhesion-promoting layer is formed.

It is still another further object of the present invention to provide a structure of a high-permittivity material/noble metal substrate laminate by sandwiching a noble metal oxide layer formed in a top surface of the noble metal substrate for providing improved adhesion and interface properties of the high-permittivity material.

It is yet another further object of the present invention to provide a method for forming a DRAM capacitor or ferroelectric memory element by first exposing the top surface of a first electrode to an oxygen-containing energy source for a sufficient length of time until an

oxygen-containing surface layer is formed such that the adhesion and interface properties of a high-permittivity dielectric or ferroelectric material subsequently deposited on the noble metal contained in the first electrode are improved.

It is yet another further object of the present invention to provide a DRAM capacitor or ferroelectric memory element that includes a layer of an interface-enhancing material formed in a top surface of a first electrode and sandwiched between a layer of a high-permittivity dielectric material and a noble metal contained in the first electrode.

Summary of the Invention

In accordance with the present invention, a method for forming a noble metal oxide layer on a noble metal substrate is provided which includes the step of exposing a surface of the noble metal substrate to an oxygen-containing plasma energy source or ion beam for a sufficient length of time until a noble metal surface oxide layer is formed.

In a preferred embodiment, a method for forming a noble metal oxide layer on a noble metal substrate can be carried out by the operating step of exposing a surface of the noble metal substrate to an oxygen-containing plasma energy source or ion beam such that a noble metal oxide adhesion-promoting layer is formed. The oxygen-containing energy source utilized can be selected from a high-density plasma, a microwave plasma, a RF plasma, an ion bombardment produced by oxygen-containing ion beams, and or combinations thereof, with or without separately controllable substrate bias. The plasma process can be carried out in a

reaction chamber that has an oxygen pressure between about 5 m Torr and about 2,000 m Torr, wherein an oxygen-containing plasma discharge is generated by a radio frequency power of at least 50 watts. For remote oxygen-containing energy sources, such as those employed in downstream microwave ashers or ion beam sources, the chamber pressure may preferably be even lower, in the range between about 0.01 m Torr and about 5 m Torr. The surface of the noble metal substrate is preferably exposed to the oxygen-containing plasma discharge for an exposure time of at least 1 second. A suitable noble metal substrate is formed by at least one noble metal from the group of Pt, Pd, Ir, Ag, Au, Ru, Os and Rh. The noble metal substrate may also be formed by a noble metal alloy selected from the above described group of metals.

The present invention is further directed to a noble metal oxide film that is formed by exposing the surface of a noble metal substrate to an oxygen-containing plasma discharge. The noble metal oxide film formed by such process typically has a thickness between about 0.4 and 10 nm, although lower and higher thicknesses may be obtained with variations in treatment conditions.

In another preferred embodiment, the present invention provides a novel method for depositing a high-permittivity or ferroelectric material on a noble metal substrate which can be carried out by the operating steps of first providing a noble metal substrate, then exposing a top surface of the noble metal substrate to an oxygen-containing energy source for a sufficient length of time until an interface-enhancing layer is formed, and then depositing a high-permittivity or ferroelectric material on top of the noble metal substrate with the interface

enhancing layer sandwiched thereinbetween. The energy source utilized is an oxygen-containing plasma which can be selected from a high-density plasma, a microwave plasma, a RF plasma and an ion bombardment produced by ion beams. The high-permittivity or ferroelectric material is a high dielectric constant material selected from the group consisting of barium strontium titanate, lead lanthanum titanate, lead zirconium titanate, bismuth titanate and other dielectric or ferroelectric perovskites.

The present invention is further directed to a structure of a high permittivity or ferroelectric material/noble metal substrate laminate which includes a noble metal substrate that has a top surface, a noble metal oxide layer formed in the top surface of the noble metal substrate, and a high-permittivity or ferroelectric material deposited on top of the noble metal substrate with the noble metal oxide layer sandwiched thereinbetween.

In still another preferred embodiment, the present invention provides a novel method for forming a DRAM capacitor which can be carried out by the operating steps of first providing a pre-processed semiconductor substrate, forming a first electrode with a first noble metal material, exposing a top surface of the first electrode to an energy source for a sufficient length of time until an interface-enhancing layer is formed, depositing a high-permittivity dielectric material on top of the first electrode with the interface-enhancing layer sandwiched thereinbetween, and forming a second electrode by a second noble metal material on top of the high-permittivity dielectric material layer. The pre-processed semiconductor substrate has a silicon contact plug that is formed therein for establishing electrical communication with the first

electrode. The adhesion-promoting layer formed is an oxide of the first noble metal.

The present invention is further directed to a DRAM capacitor that includes a pre-processed semiconductor substrate, a first electrode of a first noble metal material formed on the substrate, a layer of an interface-enhancing material formed in a top surface of the first electrode, a layer of high-permittivity dielectric material on top of the first electrode with the interface-enhancing layer sandwiched thereinbetween, and a second electrode of a second noble metal material formed on top of the high-permittivity dielectric material layer. The first electrode is a bottom electrode for the capacitor and the second electrode is a top plate electrode for the capacitor. The interface-enhancing layer contains oxygen and would typically be an oxide of the first noble metal.

Brief Description of the Drawings

Other objects, features and advantages of the present invention will be come apparent upon consideration of the specification and the appended drawings, in which:

Figure 1 is an enlarged, cross-sectional view of a conventional DRAM capacitor structure.

Figure 2A is an enlarged, cross-sectional view of a present invention substrate having a noble metal film deposited on top.

Figure 2B is an enlarged, cross-sectional view of the present invention structure shown in Figure 2A having a noble metal oxide layer formed on top by a plasma oxidation process.

Figure 3A is an enlarged, cross-sectional view of the present invention structure of Figure 2B coated with an overlayer of a high-permittivity material.

Figure 3B is an enlarged, cross-sectional view of the present invention structure of Figure 3A having a top electrode formed of a second noble metal on top.

Figure 4 is an enlarged, cross-sectional view of a present invention structure having a layer of a spin-on-glass material deposited on top of a layer of noble metal oxide.

Figure 5A is a schematic showing a direct write process for patterning a noble metal film.

Figure 5B is a schematic illustrating a reflectivity vs. position trace for the dashed line scan across the patterned area of Figure 5A.

Detailed Description of the Preferred Embodiments

The present invention discloses a method for forming a noble metal oxide layer on a noble metal substrate by exposing a surface of the noble metal substrate to an oxygen-

containing energy source. The oxygen-containing energy source may be chosen from one of the following energy sources, a high-density plasma, a microwave plasma, a RF plasma, an ion bombardment produced by oxygen containing ion beams, or combinations thereof, with or without separately controllable substrate bias. The method can be conducted in a reaction chamber that has an oxygen pressure between about 5 m Torr and about 2,000 m Torr, wherein an oxygen-containing plasma discharge can be generated by a radio frequency of at least 50 W. For remote oxygen-containing energy sources, such as those employed in downstream microwave ashers or ion beam sources, the chamber pressure may preferably be even lower, in the range between about 0.01 m Torr and about 5 m Torr. The surface of the noble metal substrate can be exposed to an oxygen-containing plasma discharge for an exposure time of at least 1 second, and preferably for at least 0.5 to 5 minutes. The noble metal can be at least one member selected from the group of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh. The noble metal substrate may also be formed by a noble metal alloy containing at least one of these noble metals. The present invention also discloses a noble metal oxide film that is formed by exposing the surface of a noble metal substrate to an oxygen-containing plasma. The noble metal oxide film formed typically has a thickness between about 0.4 and 10 nm, although lower and higher thicknesses may be obtained with variations in treatment conditions.

The present invention also discloses a novel method for depositing a high-permittivity or ferroelectric material on a noble metal substrate by first exposing a top surface of the noble metal substrate to an oxygen-containing energy source for a sufficient length of time

until an interface-enhancing layer is formed and then depositing a high-permittivity or ferroelectric material on top of the noble metal substrate sandwiching the interface-enhancing layer. The energy source utilized can be an oxygen-containing plasma. The present invention is also a structure of a high-permittivity or ferroelectric material/noble metal substrate laminate that includes a noble metal oxide layer formed in a top surface of a noble metal substrate and a high-permittivity or ferroelectric material deposited on top of the noble metal substrate sandwiching the noble metal oxide layer.

The present invention further discloses a novel method for forming a DRAM capacitor by first exposing a top surface of a first electrode that is formed of a first noble metal material to an oxygen-containing energy source for a sufficient length of time such that an interface-enhancing layer is formed, and then depositing a high-permittivity material on top of the first electrode sandwiching the adhesion-promoting layer. A final electrode is then formed with a second noble metal material on top of the high-permittivity dielectric material layer. The capacitor is formed on a pre-processed semiconductor substrate which has a silicon contact plug formed therein for providing electrical communication with the first electrode. The present invention is also a novel DRAM capacitor that has a layer of an interface-enhancing material formed in a top surface of a first electrode of a first noble metal material, and a layer of a high-permittivity dielectric material on top of the first electrode sandwiching the interface-enhancing layer. The DRAM capacitor further includes a second electrode formed of a second noble metal material and positioned on top of the high-permittivity dielectric material layer.

The present invention further discloses an optical storage medium that includes a platinum substrate and a patterned platinum oxide layer formed in a top surface of the platinum substrate. The patterned platinum oxide layer can be formed by selectively exposing a top surface of the substrate to an oxygen-containing energy source. Alternatively, the platinum oxide may be formed over the entire substrate area and then patterned by spatially selective removal.

It is generally known that noble metals such as platinum do not readily oxidize, and that the platinum oxides decompose to elemental $\text{Pt} + \text{O}_2$ at moderately elevated temperatures. It is the unique discovery of the present invention that a platinum oxide film can be formed on a platinum surface when exposed to the energetic environment of an oxygen plasma. The present invention novel method therefore discloses exemplary plasma conditions for producing platinum and iridium oxides. The characteristics of the resulting oxide films are determined by a technique of X-ray photoelectron spectroscopy (XPS).

It was discovered that a variety of plasma oxidation conditions can be used to form oxide coatings on noble metal substrates or on electrode surfaces. Different oxide stoichiometries are formed at different plasma pressures. Referring now to Figures 2A and 2B, wherein an enlarged, cross-sectional view of a present invention structure 30 is shown. As shown in Figure 2A, a noble metal film 32 is first deposited on a substrate 34. The noble metal film may be deposited of a noble metal or a noble metal alloy containing at least one noble metal selected from the group of noble metals including Pt, Pd, Ir, Ag, Au, Ru, Os and Rh. The substrate 34 may be formed of SiO_2 on silicon, or, more preferably, of a conductive material which is

resistant to oxidation and does not react with the noble metal or with an underlying silicon layer (not shown). The metal layer 32 is normally deposited on substrate 34 by a sputtering technique. A noble metal oxide layer 36 is formed in the surface layer of the noble metal film 32 by exposing the film to an oxygen-containing plasma. This is shown in Figure 2B. The oxygen-containing plasma utilized in the present invention method can be suitably provided by most commercial ashing or etching tools. For instance, a Plasmalab® μ -P-RIE 80 RIE tool or a March® Jupiter III plasma asher. The various oxidation conditions are shown in Table 1.

Table 1

Machines Test Metal Substrate	PlasmaLab® 20 mTorr, 150 W	PlasmaLab® 500 mTorr, 250 W	March® 500 mTorr, 100 W
Pt	PtO-like 2.5-3.5 nm	PtO ₂ 3.0-4.3 nm	PtO ₂ 4.0-5.0 nm
Ir	IrOx 2.5-3.5 nm	IrO ₂ 3.5-4.9 nm	—————

Table 1 shows the oxide stoichiometries and the thicknesses for platinum oxides and iridium oxides produced after 10 minutes of oxygen plasma exposure in a March tool which has a 15 cm diameter cathode, or a PlasmaLab RIE tool which has a 24 cm diameter cathode. The PlasmaLab tool is a parallel plate reactive ion etching system. Noble metal samples consisting of 100 nm of electron-beam evaporated Pt or Ir deposited on thermally oxidized silicon substrates were placed on the bottom electrode which is driven by a 13.56 MHz power supply. The process gas utilized in the chamber is O₂ at a chamber pressure of 20 mTorr obtained at a

20 sccm flow rate, or at a pressure of 500 m Torr obtained at a 50 sccm flow rate. The 20 mTorr process utilized relatively low power of 0.33 W/cm^2 , resulting in a self-bias of approximately 280-300 V. On a platinum substrate, the process produced PtO with a thickness range of between about 2.5 and about 3.5 nm. The PtO thickness is independent of treatment time over the 1 to 20 min time range examined. This suggests that the PtO quickly reaches a steady-state thickness whose value reflects a competition between PtO formation (via Pt reactions with energetic oxygen species formed in the plasma) and PtO etching (via sputtering by energetic oxygen ions formed in the plasma). The 500 mTorr process utilizes a higher power of 0.55 W/cm^2 , resulting in a self-bias of 220 V. On the platinum substrate, 10 minutes of the process produce a thicker platinum oxide film that has a composition closer to PtO at a thickness between about 3.0 and about 4.3 nm. On an iridium substrate, these processes produced iridium oxide films that had thicknesses in the range between about 2.5 and about 4.9 nm and a stoichiometry ratio close to IrO_2 .

A qualitative indication of the length of treatment time required to form the steady-state thickness of noble metal oxide can be obtained from in-situ laser reflectance measurements during oxygen plasma treatment. Clean Pt films monitored by a 633 nm HeNe laser at normal incidence during the 20 m Torr oxygen plasma treatment showed a steadily decreasing reflectance that leveled off at a 5% reflectivity loss after about 30 seconds of treatment. Exposing the oxidized Pt surface to a fluorine-based plasma treatment restored the clean Pt surface and reversed the reflectivity loss. Based on this data, the minimum required treatment time is expected to be about 30 seconds for the 20 m Torr process. However, the minimum required

treatment time would be expected to depend on the plasma oxidation conditions. Times much shorter than 30 seconds, perhaps as low as 1 sec, might be anticipated for higher density plasma conditions.

In another commercial tool, a March® Jupiter III plasma asher, the plasma oxidation of platinum surfaces was conducted by first exposing a bare noble metal surface to an oxygen plasma discharge at an oxygen pressure in the range between about 100 and about 900 m Torr, at a RF power of about 100 W (over a 15 cm diameter cathode), and for an exposure time of about 10 minutes.

While the plasma oxidation method has been described in terms of techniques of plasma ashing, i.e., a low temperature, low-substrate-bias plasma treatment in oxygen, and reactive ion etching, i.e., a plasma treatment at moderate to high substrate bias, the present invention novel method is not limited to the utilization of these exemplary plasma oxidation processes. For instance, the oxygen feed gas for the plasma can be substituted by oxygen-containing gases such as diatomic or polyatomic gases which contain oxygen as an atomic constituent, i.e., N_2O , or gas mixtures containing oxygen or one or more oxygen-containing gases such as an Ar/O_2 mixture. Additionally, various kinds of oxygen-containing energy sources may also be used which include high density plasmas, microwave plasmas, RF plasmas and ion bombardment produced by oxygen-containing ion beams. Similarly, the noble metals may be deposited by techniques other than electron beam evaporation, for instance, techniques such as sputtering, chemical vapor deposition and electrolytic or electroless plating.

The noble metals utilized in the present invention novel method may be pure noble metals, such as Pt, Pd, Ir, Ag, Au, Ru, Os and Rh, or alloys of noble metals with noble metals, alloys of noble metals with non-noble metals, alloys of noble metals with non-metals, or any layered combinations of these metals or alloys.

Example 1

A first application for the noble metal oxides formed by the present invention novel method is to improve the electronic properties of high permittivity materials deposited on noble metal electrodes in an electronic device. The high permittivity oxide materials include high-epsilon materials such as barium strontium titanate (BST), lead lanthanum titanate (PLT) and barium zirconium titanate (BZT), ferroelectric materials such as lead zirconium titanate (PZT), strontium bismuth tantalate (SBT), strontium bismuth niobate (SBN) and bismuth titanate and other perovskites. It has been found that exposing noble metal electrodes to an oxygen plasma oxygenates the noble metal surfaces by providing a surface oxide layer as described above. This process produces improved dielectric properties in the high-permittivity material deposited on such activated surfaces and also leads to improved mechanical and chemical properties. For instance, the electrical properties of specific high-epsilon films deposited by a sol-gel process on the oxidized platinum electrodes of Figure 2B are superior to those deposited on the unoxidized electrodes of Figure 2A.

In Figure 3A, a plasma-oxidized noble metal film 32 is coated with an overlayer of a high-permittivity material 38. The structure 30 of Figure 3A is then completed as a

capacitor having a top electrode layer 42 deposited on top. As an logical extension of the present invention method, improvement is also expected for metal oxides such as MgO and Al_2O_3 , which typically deposit with poor oxygen stoichiometry and more generally, for oxygen-containing materials selected from the group consisting of metal oxide insulators, metal oxide semiconductors, metal oxides conductors, metal oxide superconductors, perovskites, metal-containing silicates, SiO_2 , high-permittivity materials that have epsilon above 10, and ferroelectrics. By depositing these materials on the noble metal oxides, extra oxygen is provided to result in a proper composition.

To further prove the effectiveness of the present invention method, nominally identical 4-layer BST films having 90 nm total thickness were deposited sequentially on an un-ashed Pt/Ti/ SiO_2 substrate and an ashed (in a March tool for 10 min) Pt/Ti/ SiO_2 substrate. The BST was deposited from a 0.2 M solution of barium, strontium, and titanium 2-methoxyethoxides diluted with isopropanol to 0.1 M for spinning 215 Å layers. Each layer was sequentially hot plate dried under a typical condition of 300°C for 3 min, and then crystallized by rapid thermal annealing in atmospheric pressure oxygen under a typical conditions of 700°C for 1 min. The BST film on the un-ashed Pt substrate was characterized by a dielectric constant of 167, and a high loss tangent. The BST film on the ashed Pt substrate was characterized by a dielectric constant of 214, and an acceptably low loss tangent. These results obtained are typical in that BST usually produces better results on ashed Pt substrates.

The PLT films also produce better results on ashed electrodes. For this material,

dielectric constants in excess of 500 are achieved on ashed Pt and Ir electrodes, while lower values often result on un-ashed Pt and Ir electrodes. Some improvements in leakage current have also been observed.

Example 2

A second application for the noble metal oxides formed by the present invention novel method is to improve adhesion between deposited films and the noble metals on which they are deposited. For example, good adhesion to a noble metal substrate surface might be desired for conductive nitrides such as TiN, TaN and TaSiN; dielectric oxides such as silicon oxide; dielectric nitrides such as silicon nitride and silicon oxynitride; and carbon-containing dielectrics. Adhesion enhancement has been demonstrated for the specific use of a spin-on-glass overlayer on a platinum film substrate. Similar effects are expected for films of other materials deposited from solution, e.g., photoresists, or films deposited by chemical vapor deposition processes, e.g., SiO₂ formed by low pressure chemical vapor deposition (LPCVD) from a tetraethoxysilane (TEOS) precursor. Such a structure 50 is shown in Figure 4 wherein a plasma oxidized noble metal film 32 is covered by an overlayer of adhesion-promoting material 36. The platinum film 32 was prepared by a sequential room temperature evaporation of 100 Å Ti (not shown) and 1,000 Å Pt on a thermally oxidized (100 nm) silicon substrate 34. Adhesion layer 36 was either 100Å of sputter deposited titanium or a platinum oxide layer that was prepared by applying one of two oxygen RIE treatments in a PlasmaLab[®] tool, in either a 20 m Torr pressure process for 3 minutes (with 20 sccm O₂ flow rate, 0.33 W/cm² of power density and 300 V self bias) or a 500 m Torr pressure process for 10 minutes (with 50 sccm O₂ flow rate, 0.55 W/cm²

power density, and 220 V self bias). Test results from a XPS indicate that the PtO layer thickness was approximately 2.5~3.5 nm for the 20 m Torr process and 3.0~4.3 nm for the 500 m Torr process.

The spin-on-glass layer 46 deposited was a Hitachi HSG 2209-S7 material. The conditions for the deposition were 5,000 rpm spinning speed, 0.5 sec ramp, 3 min 90°C bake, 12 min 100°C oven bake, 125 to 450°C ramp at 5~10 °C/min in N₂ with a non-ramped cool-down.

The adhesion of an approximately 1 µm thick layer of Hitachi HSG 2209-S7 to a 100 nm platinum layer was compared for the cases of Pt with no adhesion layer and Pt with one of the three different adhesion layers described above, i.e., platinum with a 10 nm overlayer of Ti, and platinum with the plasma oxidation treatment at 20 and 500 m Torr. After a standard thermal curing process by ramping up to 450°C in N₂, the HSG on untreated platinum became cloudy and wrinkled in patches which expanded over a period of 2~3 days to cover the complete wafer surface, and was easily removed by Scotch tape. In contrast, the HSG on Ti-treated and both plasma-oxidized platinum samples remain smooth and adherent even after scratching through the film and attempting to peel it off with Scotch tape. While PtOx and Ti both function as adhesion-promoting layers, the PtOx processing is not only simpler, but also avoids potential problems with Pt/Ti diffusion reaction. It is also expected that adhesion enhancement can be obtained for both oxide and non-oxide materials deposited by more energetic techniques such as plasma-assisted chemical vapor deposition (PACVD) and reactive sputtering. In some cases, the

oxygen treatment of the noble metal substrate surface to form the adhesion-enhancing noble metal oxide layer may even be carried out concurrently with the initial steps of the deposition process if the process gases comprise an oxygen-containing species. For example, the process of depositing silicon oxide on a noble metal substrate by PACVD from a mixture of TEOS and oxygen (or by reactive sputtering of a silicon target in an oxygen-containing working gas) is likely to result in the un-intentional (but beneficial) formation of an adhesion-promoting noble metal oxide.

Example 3

In addition to the improvements in adhesion and electronic properties of the deposited materials, the present invention novel noble metal oxide films also provide benefits in optical storage and selective catalysis. Relative to the un-oxidized platinum films, the oxidized films are browner in color and lower in reflectivity. For instance, the drop in reflectivity is approximately 5% when measured by a 633 nm HeNe laser at normal incidence angle. The differences suggest the possibility of using PtOx on platinum system as an optical storage medium. Since heating the films up to 450~550 °C in an oxygen-poor environment would be expected to cause PtOx to lose oxygen and revert to elemental Pt, it is expected that the same reaction can be made to occur in a spatially selective manner by locally heating or exciting selected regions of PtOx with an electron or photon beam. This is shown in illustrations in Figures 5A and 5B.

Figure 5A illustrates a schematic for a direct write process for patterning a noble

metal film, while Figure 5B illustrates a reflectivity vs. position trace for the dashed line shown across the patterned area of Figure 5A. An oxide-free feature 60 is written on the PtOx surface 54 with a directed energy source 56, for example, a focused laser or electron beams. Spatially selective catalysis could therefore be achieved if the same patterning techniques were used to define activated or non-activated regions of an oxidized noble metal surface.

It should be noted that, in addition to the above described benefits and advantages achievable by the present invention method, the surface wetting and uniformity characteristics are also enhanced by a plasma ashing or oxidation process. This has been demonstrated for sol-gel deposited films of high dielectric constant materials such as BST and PLT, and also for ferroelectric materials such as bismuth titanate on substrates consisting of platinum electrodes separated by field regions of silicon oxides.

In recent years, the invention of new microscopies that have near atomic resolution, i.e., the scanning tunneling microscopy (STM), the atomic force microscopy (AFM) and the scanning interferometric apertureless microscopy (SIAM) has triggered a flurry of activities in finding new methods for storing information with ultra-high data density. In this regard, the problem of finding a suitable method for achieving high density read-only storage schemes seems more readily solvable and therefore, may provide solutions for permanent storage of large amount of data such as that contained in the Library of Congress. By using these techniques, bits can be made on a surface by means of STM's and AFM's, although currently at relatively low speeds, while high density reading can be done faster by means of the SIAM.

A practical way of writing bits with high density can be derived from distinct catalytic properties selected surface sites, so that material that creates optical contrast can be selectively deposited by means of CVD techniques. Due to the known catalytic properties of metals such as Pt and Pd, a method that locally shields such metals can be used to selectively deposit material on the uncovered regions by means of a CVD process. For instance, surface oxidation of these metallic surfaces in the form of a very thin oxide layer can prevent the catalytic effect.

While the present invention has been described in an illustrative manner, it should be understood that the terminology used is intended to be in a nature of words of description rather than of limitation.

Furthermore, while the present invention has been described in terms of several preferred embodiments, it is to be appreciated that those skilled in the art will readily apply these teachings to other possible variations of the inventions.

Claims

1. A method for forming an noble metal oxide film layer on and at least partially covering a surface of a noble metal substrate comprising the steps of exposing said surface of the noble metal substrate to an oxygen-containing plasma.
2. A method according to claim 1 further comprising the step of feeding a plasma with at least one oxygen-containing gas.
3. A method according to claim 1, wherein said oxygen-containing plasma is selected from the group consisting of a high-density plasma, a microwave plasma, a RF plasma and an ion bombardment produced by oxygen-containing ion beams or combinations thereof, with or without separately controllable substrate bias.
4. A method according to claim 1; wherein said method is conducted in a reaction chamber having an oxygen pressure between about 0.01 m Torr and about 2,000 m Torr.
5. A method according to claim 1, wherein said oxygen plasma discharge is generated by a radio-frequency power of at least 50 W.
6. A method according to claim 1, wherein said surface of the noble metal substrate is exposed to an oxygen plasma discharge for an exposure time of at least 1 second.



7. A method according to claim 1, wherein said noble metal substrate comprises at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

8. A method according to claim 1, wherein said noble metal substrate comprises a noble metal alloy consisting of at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

9. A method according to claim 1, wherein said noble metal substrate comprises two or more layers of noble metals each selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

10. A noble metal oxide film layer formed by exposing the surface of a noble metal substrate to an oxygen-containing plasma.

11. An oxygen-containing film layer according to claim 10, wherein said film layer having a thickness between about 0.4 nm and about 10 nm.

12. An oxygen-containing film layer according to claim 10, wherein said oxygen-containing plasma is selected from the group consisting of a high-density plasma, a microwave plasma, a RF plasma, an ion bombardment produced by oxygen-containing ion beams and combinations thereof, with or without separately controllable substrate bias.



13. An oxygen-containing film layer according to claim 10, wherein said oxygen plasma discharge is generated by a radio-frequency power of at least 50 W.

14. An oxygen-containing film layer according to claim 10, wherein said surface of the noble metal substrate is exposed to an oxygen plasma discharge for an exposure time of at least 1 second.

15. An oxygen-containing film layer according to claim 10, wherein said noble metal substrate comprises at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

16. An oxygen-containing film layer according to claim 10, wherein said noble metal substrate comprises a noble metal alloy consisting of at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

17. An oxygen-containing film layer according to claim 10, wherein said noble metal substrate comprises two or more layers of noble metals each selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.



18. A method for depositing an oxygen-containing material on a noble metal substrate comprising the steps of:

providing a noble metal substrate,

exposing a top surface of the noble metal substrate to an oxygen-containing energy source for a sufficient length of time until an interface-enhancing layer is formed, and

depositing an oxygen-containing material on top of said noble metal substrate with said interface-enhancing layer sandwiched thereinbetween.

19. A method according to claim 18, wherein said oxygen-containing energy source is a plasma source.

20. A method according to claim 18, wherein said oxygen-containing energy source is an oxygen-containing plasma.

21. A method according to claim 18, wherein said oxygen-containing energy source is an oxygen-containing plasma selected from the group consisting of a high-density plasma, a microwave plasma, a RF plasma and an ion bombardment produced by oxygen-containing ion beams or combinations thereof, with or without separately controllable substrate bias.

22. A method according to claim 18, wherein said step of exposing said top surface of the noble metal substrate to an energy source is conducted in a reaction chamber



having an oxygen pressure between about 0.01 m Torr and about 2,000 m Torr.

23. A method according to claim 18, wherein said noble metal substrate comprises at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

24. A method according to claim 18, wherein said sufficient length of time is at least 1 second.

25. A method according to claim 18, wherein said noble metal substrate comprises a noble metal alloy consisting of at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

26. A method according to claim 18, wherein said oxygen-containing material is a perovskite-type insulator material.

27. A method according to claim 18, wherein said oxygen-containing material is selected from the group consisting of barium strontium titanate (BST), lead lanthanum titanate (PLT), lead zirconium titanate (PZT), barium zirconium titanate (BZT), strontium bismuth tantalate (SBT), strontium bismuth niobate (SBN), and bismuth titanate.

28. A method according to claim 18, wherein said oxygen-containing material is selected from the group consisting of metal oxide insulators, metal oxide semiconductors, metal



oxide conductors, metal oxide superconductors, metal-containing silicates, silicon oxide, high-permittivity materials having epsilon of greater than 10 and ferroelectrics.

29. A method according to claim 18, wherein said interface-enhancing layer formed is an oxide of the noble metal contained in the noble metal substrate.

30. A method according to claim 18, wherein said interface-enhancing layer formed has a thickness between about 0.4 nm and about 10 nm.

31. A structure of an oxygen-containing material/noble metal substrate laminate comprising:

a noble metal substrate having a top surface,
a noble metal oxide layer in a top surface of said noble metal substrate, and
an oxygen-containing material deposited on top of said noble metal substrate with said noble metal oxide layer sandwiched thereinbetween.

32. A structure according to claim 31, wherein said noble metal oxide layer is an interface-enhancing layer having a thickness between about 0.4 nm and about 10 nm,

33. A structure according to claim 31, wherein said oxygen-containing material is a high dielectric constant material selected from the group consisting of barium strontium titanate (BST), lead lanthanum titanate (PLT), lead zirconium titanate (PZT), barium zirconium



titanate (BZT), strontium bismuth tantalate (SBT), strontium bismuth niobate (SBN), and bismuth titanate.

34. A structure according to claim 31, wherein said oxygen-containing material is a Perovskite-type insulator material.

35. A structure according to claim 31, wherein said oxygen-containing material is selected from the group consisting of metal oxide insulators, metal oxide semiconductors metal oxide conductors, metal oxide superconductors, metal-containing silicates, silicon oxide, high-permittivity materials having epsilon of greater than 10 and ferroelectrics.

36. A structure according to claim 31, wherein said noble metal substrate comprises at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

37. A structure according to claim 31, wherein said noble metal substrate comprises a noble metal alloy consisting of at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

38. A method for forming a semiconductor memory element comprising the steps of:

providing a pre-processed semiconductor substrate,



forming a first electrode with a first noble metal material,
exposing a top surface of said first electrode to an oxygen-containing energy source for a sufficient length of time to form an interface-enhancing layer,

depositing a high-permittivity dielectric or ferroelectric material on top of said first electrode with said interface-enhancing layer sandwiched thereinbetween, and

forming a second electrode with a second noble metal material on top of said high-permittivity dielectric or ferroelectric material layer.

39. A method according to claim 38, wherein said pre-processed semiconductor substrate having a conductive contact plug formed therein adapted for electrical communication with said first electrode.

40. A method according to claim 38, wherein said first noble metal material and said second noble metal material are selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

41. A method according to claim 38, wherein said first noble metal material and said second noble metal material are formed of a noble metal alloy consisting of at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.



42 A method according to claim 38 wherein said first noble metal material is the same as the second noble metal material.



43. A method according to claim 38 wherein said oxygen-containing energy source is an oxygen-containing plasma.

44. A method according to claim 38, wherein said oxygen-containing energy source is an oxygen-containing plasma selected from the group consisting of a high-density plasma, a microwave plasma, a RF plasma and an ion bombardment produced by oxygen-containing ion beams or combinations thereof, with or without separately controllable substrate bias.

45. A method according to claim 38, wherein said step of exposing a top surface of said first electrode to an energy source is conducted in a reaction chamber having an oxygen pressure between about 0.01 m Torr and about 2,000 m Torr.

46. A method according to claim 38, wherein said sufficient length of time is at least 1 second.

47. A method according to claim 38, wherein said high -permittivity or ferroelectric material is a perovskite-type insulator material.



48. A method according to claim 38, wherein said high-permittivity or ferroelectric material is a high dielectric constant material selected from the group consisting of barium strontium titanate (BST), lead lanthanum titanate (PLT), lead zirconium titanate (PZT), barium zirconium titanate (BZT), strontium bismuth tantalate (SBT), strontium bismuth niobate (SBN) and bismuth titanate.

49. A method according to claim 38, wherein said high-permittivity or ferroelectric material is selected from the group consisting of metal oxide insulators, metal-containing silicates, silicon oxide, high-permittivity materials having epsilon of greater than 10 and ferroelectrics.

50. A method according to claim 38, wherein said interfacing-enhancing layer formed is an oxide of said first noble metal material.

51. A method according to claim 38, wherein said interfacing-enhancing layer formed has a thickness between about 0.4 nm and about 10 nm.

52. A method according to claim 38, wherein at least one of said first and second electrodes is formed by two or more layers of noble metal material selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.



53. A semiconductor memory element comprising:

- a pre-processed semiconductor substrate,
- a first electrode of a first noble metal material on said substrate,
- a layer of an interfacing-enhancing material in a top surface of said first electrode,
- a layer of high-permittivity dielectric or ferroelectric material on top of said first electrode with said adhesion-promoting layer sandwiched thereinbetween, and
- a second electrode of a second noble metal material on top of said high-permittivity dielectric or ferroelectric material layer.

54. A semiconductor memory element according to claim 53, wherein said pre-processed semiconductor substrate having a silicon contact plug formed therein adapted for electrical communication with said first electrode.

55. A semiconductor memory element according to claim 53, wherein said first noble metal material and said second noble metal material are selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.

56. A semiconductor memory element according to claim 53, wherein said first noble metal material and said second noble metal material are formed of a noble metal alloy consisting of at least one noble metal selected from the group consisting of Pt, Ir, Ag, Au, Ru, Pd, Os and Rh.



57. A semiconductor memory element according to claim 53, wherein said first noble metal material is the same as the second noble metal material.

58. A semiconductor memory element according to claim 53, wherein said adhesion-promoting layer is an oxide of said first noble metal material.

59. A semiconductor memory element according to claim 53, wherein said high-permittivity material is a perovskite-type insulator material.

60. A semiconductor memory element according to claim 53, wherein said high-permittivity material is a high dielectric constant material selected from the group consisting of barium strontium titanate (BST), lead lanthanum titanate (PLT), lead zirconium titanate (PZT) and bismuth titanate.

61. A semiconductor memory element according to claim 53, wherein said adhesion-promoting layer formed has a thickness between about 0.4 nm and about 10 nm.

62. A semiconductor memory element according to claim 53, wherein said first electrode is a bottom electrode for the capacitor and said second electrode is a top plate electrode for the capacitor.



63. An optical storage medium comprising:

a platinum substrate, and

a platinum oxide layer formed in a top surface of said platinum substrate.

64. An optical storage medium according to claim 63, wherein said platinum oxide layer is patterned by exposing a top surface of said substrate to a directed energy source.

65. A method for depositing a material on a noble metal substrate comprising the steps of:

providing a noble metal substrate,

exposing a top surface of the noble metal substrate to an energy source for a sufficient length of time until an adhesion-promoting layer is formed, and

depositing a material on top of said noble metal substrate with the adhesion-promoting layer sandwiched thereinbetween.

66. A method according to claim 65, wherein said energy source is an oxygen-containing plasma selected from the group consisting of a high-density plasma, a microwave plasma, a RF plasma, an ion bombardment produced by oxygen-containing ion beams and combinations thereof, with or without separately controllable substrate bias.



67. A method according to claim 65, wherein said material deposited is a spin-on-glass material or photoresist.

68. A method according to claim 65, wherein said material deposited is selected from the group consisting of conductive nitrides of TiN, TaN and TaSiN, dielectric oxides of silicon, oxide, dielectric nitrides of silicon nitride, silicon oxynitride, and carbon-containing dielectrics.

69. A structure of a material/noble metal substrate laminate comprising:
a noble metal substrate having a top surface,
a noble metal oxide layer formed in a top surface of the noble metal substrate, and
a material deposited on top of the noble metal substrate with the noble metal oxide layer sandwiched thereinbetween.

70. A structure according to claim 69, wherein said noble metal oxide layer is an adhesion-promoting layer having a thickness between about 0.4 nm and about 10 nm.

71. A structure according to claim 69, wherein said material in the material/noble metal substrate laminate is a spin-on-glass material.



72 A structure according to claim 69, wherein said material deposited on top of said noble metal substrate is selected from the group consisting of conductive nitrides of TiN, TaN and TaSiN, dielectric oxides of silicon oxide, dielectric nitrides of silicon nitride and silicon oxynitride and carbon-containing dielectrics.

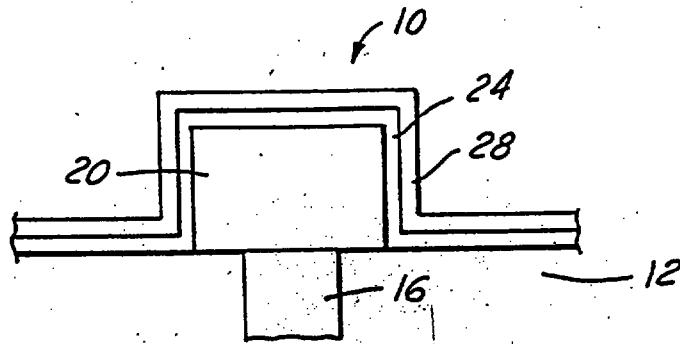
METHOD FOR FORMING NOBLE METAL OXIDES AND STRUCTURES FORMED THEREOF

ABSTRACT

The present invention discloses a method for forming a noble metal oxide film layer (32) on a noble metal substrate (34) by exposing a surface of the noble metal substrate (34) to an oxygen-containing energy source. The noble metal may also be formed as a noble metal alloy containing at least one of those noble metals. The invention also discloses a noble metal oxide film layer (36) that is formed by exposing the surface of a noble metal substrate (34) to an oxygen-containing plasma.

The invention also discloses a novel method for depositing a high-permittivity material (38) on a noble metal substrate (34) by first exposing a top surface of a noble metal substrate to an oxygen-containing energy source for a sufficient length of time until an interface-enhancing layer is formed and then depositing a high-permittivity material on top of the noble metal substrate (30) sandwiching the oxygen-containing layer (36).

Fig. 3B



PRIOR ART
FIG. 1

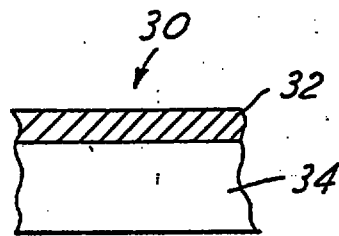


FIG. 2A

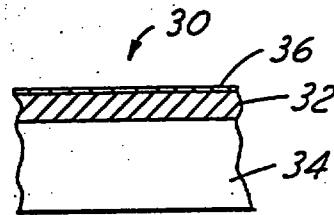


FIG. 2B

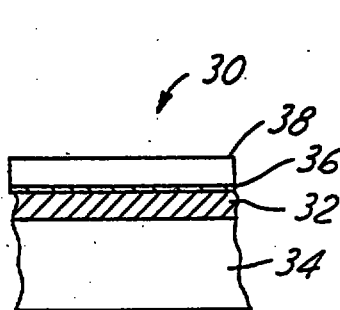


FIG. 3A

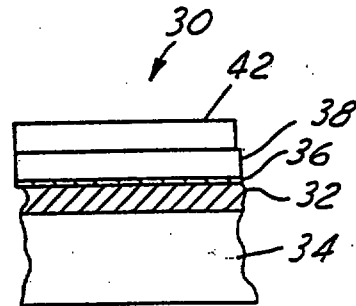


FIG. 3B

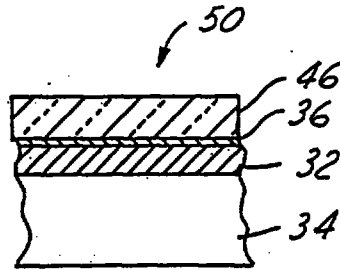


FIG.4

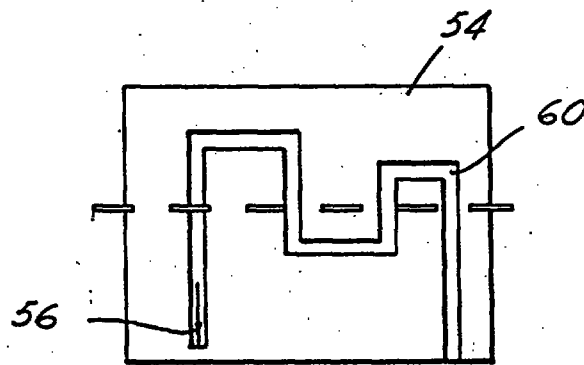


FIG.5A

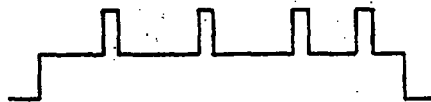


FIG.5B