Electrically active devices are formed using a special conducting material of the form Tm-Ox mixed with SiO₂ where the materials are immiscible. The immiscible materials are forced together by using high energy process to form an amorphous phase of the two materials. The amorphous combination of the two materials is electrically conducting but forms an effective barrier.

5 Claims, 1 Drawing Sheet
ELECTRICALLY CONDUCTING TERNARY AMORPHOUS FULLY OXIDIZED MATERIALS AND THEIR APPLICATION

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of the U.S. Provisional Application No. 60/126,330, filed on Mar. 22, 1999.

STATEMENT AS TO FEDERALLY SPONSORED RESEARCH

The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) in which the Contractor has elected to retain title.

BACKGROUND

Thin films are used in many devices. The stability of these devices is often determined by the degradation of the thin films and/or their interaction with adjacent materials.

Ferroelectric and high dielectric constant materials have been suggested as materials to obtain new and improved results in various applications. One application is in forming capacitors based on these materials. These eventual materials can be integrated on a chip with a silicon-based device. However, issues exist as part of integrating the material that is used. Preparation of the Ferroelectric and high dielectric materials are performed at relatively high temperatures, e.g. 400 to 800°C, in oxidizing environments. This imposes limitations on the choice of a suitable electrode material.

In addition, the use of complex compositions may cause undesired reactions, and possible deterioration of the materials. One approach to minimize undesirable interactions between such materials is to insert a barrier layer between the materials. This layer should be stable in its contact with its adjacent materials. The barrier should also hinder the diffusion of adjacent species across it. In applications where an electrical current must be able to flow across the layer, it is the case of contacts to electronic devices, the barrier layer also needs to be electrically conducting. Barriers have been used to block certain diffusion types. However, the use of a barrier results in a complex multi-layered electrode/barrier structure.

One suggested operation has been to deposit a contact on a polysilicon substrate, and to deposit a ferroelectric electrode on the contact. The deposition is done between 400 and 700°C, e.g. 500°C, using MOCVD. The deposited ferroelectric material is annealed under a partial pressure of oxygen in order to nucleate and grow a crystalline ferroelectric phase. This oxidizing environment grows the crystal at a high partial pressure of oxygen.

In the prior art, this oxygen has caused certain problems. The oxygen moves along the material, and can oxidize surfaces on the material. For example, the contact layer on the polysilicon can oxidize the silicon material. A thin layer of a non-oxidizing contact material, such as platinum, is often placed on the silicon. The platinum can itself oxidize, or material below the platinum can oxidize. The polysilicon underlayer can also oxidize. A diffusion barrier can be formed to prevent the oxygen from entering the polysilicon.

Alternatives to the platinum electrode have been suggested. A ruthenium dioxide electrode has been suggested, for example in “Electrode Structures for Integration of Ferroelectric or High Dielectric Constant Films in Semiconductor Device” Albert Grill, IBM Research Division, 1999.

SUMMARY

The present application teaches a conducting layer, formed on an electrically active structure, the conductive layer being formed of a ternary oxide material having first and second immiscible compounds, said first and second immiscible compounds having one common oxygen element, which are formed in an amorphous state, and are meta-stable relative to one another over a specified range. An embodiment describes a specific material for use in forming contacts which have specific advantageous properties; including high resistance to oxidation, electrical conductivity, and formation of a block to the passage of certain materials such as oxygen.

A specific material described herein is an electrically-conducting fully oxidized transition metal compound combined with an oxide of a different material, where the two materials are immiscible at the temperature range of interest and in combination form an amorphous material. The transition metal can be any of a number of desired transition metals, with preferred materials being ruthenium, (Ru) iridium (Ir) and osmium (Os). Other materials are described herein.

The additional oxide can be an oxide of Silicon or of another material. Silicon is preferred since the SiO2 material is generally grown on a silicon substrate which can prevent additional reactions.

On particularly interesting material is a ternary material of the type Ru—Si—O.

Another material is a ternary thin film of the type Tm—Si—O where Tm is a transition metal of the Ti, V, chromium groups.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other aspects will be described in detail with reference to the drawings in which:

FIG. 1 shows a first diagram of top contact capacitor using the specified dielectric materials;

FIG. 2 shows a diagram of a high density capacitor over bit line type using the material;

FIG. 3 show a formation technique.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Amorphous films are generally superior to polycrystalline films as barriers to diffusion. In thin polycrystalline films the mechanism of diffusion along grain boundaries or extended defects can be very fast compared to the bulk mechanisms of diffusion when the temperature is about half of the absolute melting point of the material, or below. Integrated circuits operate in that temperature range, meaning that the performance of a barrier layer depends on its microstructure and therefore on its deposition conditions. As a remedy, barrier layers have been developed in recent years that are electrically conducting and have an amorphous or near-
amorphous structure in which grain boundaries and extended defects do not exist. Their structure is also highly metastable, meaning that the nucleation and growth of crystalline grains is set only at high temperatures.

These films typically consist of an early transition metal, silicon, and nitrogen. They are normally deposited by reactive sputtering of the metal and the silicon. \( \text{Ta}_3\text{Si}_1\text{N}_{50} \), for example, crystallized only above 900°C after 30 min of heat treatment in vacuum. The combination of Ta, Si, and N in the Ta—Si—N barrier is only one case of a group of ternary nitrides that all share the same general characteristics of Ta—Si—N. These nitrides are of the generic form \( \text{TM-Si-N} \), where TM is any early transition metal from the Ti, V, or Cr group of the periodic table (the “early transition metals”). Barriers of this type have been successfully tested for electrical contacts to electrically active structures, such as solid-state devices of Si, GaAs, and/or other semiconductors. For example, the reaction between a copper overlayer on a silicon substrate can be suppressed with a Ta—Si—N barrier layer up to a record-breaking 950°C for 30 min in vacuum. These barrier layers have simultaneous amorphous or near-amorphous structure, high metastability, and chemical stability against reaction with silicon and copper.

Progress in technology and the increasing use of alternative materials has lead to processing and operation in highly oxidizing ambients. Although generally stable structurally and chemically, these ternary TM—Si—N films may react with oxygen. The resulting oxide is insulating, so that the TM—Si—N films cannot be used as barrier layers in electrical contacts of devices whose fabrication or operation exposes them to oxidizing ambients. For example, Ta—Si—N layers have been tested in contacts to ferroelectric capacitors. In that application, the barrier layer is exposed to temperatures ranging up to 800°C for duration of minutes, or at lower temperatures for extended durations. These heat treatments take place in an oxidizing ambient, not in vacuum as in the previous example of copper contacts to silicon. A problem then arises because Ta—Si—N films oxidize when heated in the presence of oxygen. A need therefore exists for thin films that share the positive attributes of TM—Si—N as diffusion barriers, but that will sustain exposures to a hot oxidizing ambient without reacting. Ternary TM—Si—O films provide a solution to this problem.

An embodiment describes specific devices that can be formed and a desired material for use in those devices. As described above, this desired material includes a first material which is an electrically conductive, fully-oxidized conducting transition metal mixed with a second material, which is another oxide material. The first and second materials are immiscible over the temperature range of interest, to form an amorphous material. A highly oxygenated ambient sphere has oxygen which can diffuse into the materials. At low temperatures, (below the so called tamont temperature) diffusion occurs along the grain boundaries of the material. The preferred system described herein uses an amorphous oxidizing conductor which can prevent diffusion since it has substantially no grain boundaries and hence may be able to prevent many of these effects.

A low density capacitor structure is shown schematically in FIG. 1. This structure is a top contact type strap capacitor. A silicon based dielectric 100 encapsulates the device and protects it during fabrication of the ferroelectric material. Specifically, the dielectric material 100 can be polysilicon. A bottom electrode 102 is formed on the dielectric. A ferroelectric or high epsilon material oxide dielectric is formed between the bottom electrode 102 and the top electrode 108. The top electrode and/or bottom electrode are preferably formed of the fully oxidized amorphous conducting material described herein.

Typically a via 110 is opened in the silicon dielectric 100 after fabrication. The via is used to connect between the electrode 110 and the transistor formed under the dielectric. This transistor/capacitor structure then effectively forms one memory cell.

A higher density is obtained by using a “capacitor over bit line” type material. These materials have more stringent requirements for the bottom electrode structure. The materials on the bottom electrode shown as 200 must maintain a conductive path between the transistor and the capacitor. In addition, the integrity of devices must be maintained during preparation, which can be in temperatures in excess of 500°C in an oxidizing environment.

The specific material described herein meets all of these requirements, is resistant to formation of an insulating oxide, remains electrically conductive after fabrication, forms a barrier to oxygen diffusion, a barrier to silicon diffusion and also does not interact with the dielectric or with the other material.

The capacitor-over-bit-line system includes a transistor 210 formed over a via 212. A conductive plug 213 fills the via and connects the transistor to a bottom electrode 200 formed of the fully oxidized material described herein. Since the capacitor is directly over the transistor, higher fill factor is obtained by this system.

The advantageous material described herein can also be used in other applications, including thick and thin film resistors, for coating on electrodes, especially in difficult environments such as oxidizing environments and space, in batteries, in electrochemical devices, catalysts, and in displays such as flat panel displays and plasma displays. These materials can also be used as contacts for high temperature superconductors.

The disclosed ternary TM—Si—O films rests on the combination of the TM—Si—N films and applying these materials to oxides. In a simplified way, Ta—Si—N films may be thought of as a combination of tantalum nitride and silicon nitride, that is, a kind of a mixture of the metallic conductor TiN and the of the insulator SiN. These two nitrides are immiscible. This immiscibility is the reason why the ternary nitrides becomes highly metastable when deposited by a process that generates a random mixture of the constituent elements. A combination of two immiscible oxides will then lead to a ternary alloy that is also highly metastable, but is already oxidized. For example, ruthenium dioxide is a metallic conductor, like tantalum nitride is, and SiO2 is an insulator, like silicon nitride is. These two oxides are also immiscible. The combination of these two compounds will thus also lead to a type of ternary Ru—Si—O alloy that is already oxidized and, by analogy with TM—Si—N films, will have properties similar to those of the TM—Si—N films. Besides RuO2, a number of other electrically conducting oxides exists, of which OSO4, RhO2, and IrO2 are closely related to RuO2. They all have the potential of forming amorphous or near-amorphous films when combined with SiO2 in the way RuO2 does. This group of materials can be described analogously to TM—Si—N alloys as ternary TM—Si—O alloys, where TM is any of the foregoing metals. CrO2, MoO2, WO3, TiO2, ReO3, and Ir2O3 are also conducting oxides and are considered as further possibilities for TM—Si—O alloy formation.

The TM—Si—O films described herein have simultaneous amorphous or near-amorphous structure, very high
metastability, and stability against reaction with noble ele-
ments and with oxidizing ambients.

The specific material is of the type Tm—Si—O where Tm
is a ternary metal of the type that forms a conducting oxide.
This ternary metal can be ruthenium (Ru), iridium (Ir),
-osmium (Os), titanium (Ti), indium (In), chromium (Cr),
tungsten (W), rhenium (Re), rhodium (Rh), or molybdenum
(Mo) with the first three listed materials being most pre-
ferred.

The material forms a metastable combination of two
immiscible oxide materials. Since the materials are
metastable, none or virtually no crystalline combinatorial
structures are formed. Used as the example of the transition
metal being ruthenium, ruthenium dioxide and silicon di-
oxide are not miscible at room temperature. If they are heated,
no ruthenium-silicon oxide crystalline phase is formed.
Therefore, the material forms an amorphous phase between
the different oxide materials. The material is metastable in
the sense that it is stable over the temperatures of interest.
When heated above the temperature of interest, the com-
bined material could disassociate.

The second immiscible oxide could be any oxide material
that forms. Silicon dioxide is preferred since many of the
semiconductor operations are carried out on a silicon sub-
strate. Any material other than silicon could also form an
undesirable silicide based on an undesired combination
between the silicon in the substrate and the other material of
the insulator.

Material Formation
The material is formed using a brute force process. If the
material were simply mixed, it would form ruthenium dioxi-
de sites and silicon dioxide sites. The system described
therein uses energy to place the two materials together in an
atomic mix. Since the materials cannot move, they effec-
tively become jammed into place. Either no crystals or very
few crystals are formed by this operation. This effectively
forms a boundary.

One way of formation is shown with reference to FIG. 3.
A conventional sputtering target 300 is formed including
ruthenium and silicon thereon. The target is sputtered using
an energized O2 gas. The oxygen in the gas combines with both
the ruthenium and silicon to form a mixed by-product.

The final materials is believed to be Ru2O3, SiO2, O2.

Alternative formation techniques use other energetic pro-
cesses to molecularly include the materials therein. Alternate formation techniques include chemical vapor deposition,
a sol-gel, deposition technique or laser ablation.

The desired material therefore takes two effectivively
immiscible oxide materials and forces them together into an
amorphous phase. This amorphous phase is meta-stable in the
sense that it stable over the temperatures of interest. Over
that temperature range, the material remains as a ternary
dimorphous oxide.

Preferred Materials
The preferred materials include RuO2+SiO2 or IrO2+SiO2.
As described above, when RuO2 is heated, it can form RuO3,
which is a volatile gas. It is believed by the inventors that
IrO2 may be in some senses superior to RuO3 since the IrO2
may not form IrO3 quite as easily.

OSO2 could also be used.

Other materials include In2O3, TiO2, CrO3, WO3, ReO3, RhO2, MoO2.

The second material can be SiO2 or any other oxide
material which is immiscible with the first material. One
example is Al2O3. The compounds that are used should have
one common element, here oxygen, but be immiscible with
one another. By forcing these two materials together, a
meta-stable amorphous phase is obtained.

The application of these novel films in contacts to ferro-
electric materials is but one example. These novel films
possess superior attributes as contacts to all oxygen-bearing
materials such as high dielectric materials, high Tc materials,
piezoelectric materials, or inorganic electroluminescent
materials. Furthermore, they offer advantages in harsh
environments, such as for electrodes of batteries, for plasma
displays, and for elements operating in corrosive environ-
ments like electrodes or resistors for thermal ink-jet printers.

Applications generally fall into one of several categories,
according to whether the novel film is to assure stability in
a material system during its formation (short-term stability
requirement), or during its use (long-term stability
requirement), of both.

The inventors intend the embodiments described above to
be examples of the general concept, and that those of skill
in the art would understand that modifications are possible.

What is claimed is:
1. An electronic capacitive device, comprising:
an electrically active structure; and
a conducting layer, formed on said electrically active
structure, said conductive layer consisting essentially
of three materials forming a ternary oxide material
having first and second immiscible compounds, said
first and second immiscible compounds having one
common element, wherein said first compound is of the
form JmOx, wherein J is a transition metal that is one
of Ru, Mo, Rh, Os, Re, W, Cr, Ti, In or Ir, and said
second compound is of the form J0y where J is a
different material than Jm and said first and second
compounds being formed in an amorphous state, and
being meta-stable relative to one another over a tem-
perature range, and wherein said common element is
oxygen, said conductive layer and said electrically
active structure collectively forming a part of a capaci-
tor.
2. A device as in claim 1
wherein said second material is SiO2.
3. A device as in claim 1,
wherein said second compound is SiO2.
4. An electronic capacitive device, comprising:
an electrically active structure; and
a conducting layer, formed on said electrically active
structure, said conductive layer consisting essentially
of three materials forming a ternary oxide material
having first and second immiscible compounds, said
first and second immiscible compounds having one
common element, which are formed in an amorphous
state, and are meta-stable relative to one another over a
temperature range, and wherein said common element
is oxygen, said conductive layer and said electrically
active structure collectively forming a part of a capaci-
tor, wherein said first material is RuO2, and said
second material is SiO2.
5. A metallic oxide material, consisting essentially of a
amorphous combination of a first material formed of SiO2,
and a second oxide material formed of RuO2, wherein said
first and second oxide materials are immiscible to form said
amorphous phase.

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