A method of reactive ion etching both a lead zirconate titanate ferroelectric dielectric and a RuO₂ electrode, and a semiconductor device produced in accordance with such process. The dielectric and electrode are etched in an etching gas of O₂ mixed with either CHCl₂CF₃ or CHF₂CCl₃.
FIG. 1

- Anode
- Substrate
- Cathode
- Gas In
- r.f.
- Pumping
- Cooling Water
- CHCIFC3
- O2
**FIG. 2**

- PZT
- Etching Rate (Å/min) vs Pressure (mTorr)
- PO₂/P tot = 0%
- PO₂/P tot = 17%
- PO₂/P tot = 25%
- PO₂/P tot = 33%
- PWR = 150 WATTS

**FIG. 2A**

- RuO₂
- Etching Rate (Å/min) vs Pressure (mTorr)
- PO₂/P tot = 0%
- PO₂/P tot = 17%
- PO₂/P tot = 25%
- PO₂/P tot = 33%
- PWR = 150 WATTS
200°C, 0.5 hr. baking after etching

PZT sample totally etched off

PZT sample before etching

XPS INTENSITY

FIG. 3
FIG. 5

- Relative at. Conc.

- Etching Time (min.)

- 30 mtorr
- 0% O₂
- 150 watts

- Pb
- Zr
- Ti

FIG. 6

- Etching Rate (Å/min.)

- Etching Power (watts)

- 30 mtorr
- 0% O₂

- PZT
In ordinary RIE, material is selectively removed by an interaction with chemically reactive ion species created by a radio frequency ("RF") glow discharge maintained in the etching chamber. RIE normally involves covering the surface to be etched with a mask which leaves exposed the selected areas to be etched. The substrate is then placed into a chamber containing a chemically reactive gas such as CF₄ mixed with O₂. A plasma is produced by applying an RF potential across the gas to dissociate and form various species including positive and negative ions, reactive atoms such as fluorine, and radicals. This plasma reacts with the unmasked and exposed surface of the material to be etched to form volatile products which are removed to leave an etched profile.

One of the barriers to widespread use of PZT ferroelectrics as a dielectric in DRAM capacitors is the difficulty of etching such materials and their associate electrodes in an effective and efficient manner. The difficulty is compounded by the difficulty of identifying a suitable etch gas that can etch all three components of the PZT solid solution (PbO, ZrO₂ and TiO₂) at an acceptable rate, and identifying a common etch gas for both the RuO₂ electrode or other electrode and the PZT ferroelectric material which will allow for stacked capacitor etching. Plasma etching of PZT thin films in CF₄ and HCl plasmas has been reported in M. R. Poor, A. M. Hurt, C. B. Fledermann and A. U. Wu, Mat. Res. Soc. Symp. Proc., 200 (1990). However, to obtain high etch rates, substrate heating was necessary in their process. RIE of RuO₂ with a CF₄/O₂ plasma has been reported in S. Saito and K. Kuramasa, Jpn. J. Appl. Phys. 31, 135 (1993). The use of CF₄-O₂ has been reported in RIE of RuO₂ (see, S. Saito and K. Kuramasa, Jpn. J. Appl. Phys. 31, 135 (1992)) and the use of CCl₄ has been reported in RIE of PZT (see, S. Saito, et al., Jpn. J. Appl. Phys. 31, L1260 (1992)). CCl₂F₂ with O₂ has been used to etch both RuO₂ and PZT films, but CCl₂F₂ is believed to be environmentally damaging. Therefore, there is a need for an environmentally safe etching gas to use in RIE of RuO₂ and PZT films.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing an apparatus for practicing the present invention.

FIG. 2 is a graph of etch rate on PZT versus etch gas pressure.

FIG. 2A is a graph of etch rate of RuO₂ versus etching gas pressure.

FIG. 2B is a graph showing the etch rate of PZT and RuO₂ films as a function of oxygen percentage.

FIG. 3 is a comparison of an ESCA wide scan before, during and after the etch process of the present invention on PZT.

FIG. 4 is a comparison of an ESCA wide scan before, during and after the etch process of the present invention on RuO₂.

FIG. 5 is a graph of the relative atomic concentration of Pb, Zr and Ti as a function of etch time for etching in accordance with the present invention.

FIG. 6 is a graph of etch rate of PZT versus RF power.

DETAILED DESCRIPTION OF THE INVENTION

PZT films can be deposited on a Pt/Ti/SiO₂/Si substrate by metalorganic decomposition (MOD) in acor-
dance with methods known in the art. See, for example, G. Yi and M. Sayer, Ceram Bull. 70(7), 1173 (1991). In a preferred embodiment of the present invention, the PZT precursor is a metalorganic solution (0.5M) of lead acetate, zirconium n-propoxide and titanium iso-
propoxide dissolved in n-propanol. The solution is spin coated on the substrate at 2000 rpm for 40 seconds and subsequently dried at 150° C. for 3 minutes. This spin-
bake cycle was repeated until the desired thickness of 2000Å was obtained. The coated PZT films were annealed at 650° C. for 30 minutes to form the perovskite phase. Similarly, RuO₂ films with thickness of 2000Å can be reductively sputtered onto a SiO₂/Si substrate in an argon-oxygen atmosphere at a gas pressure of 10 mTorr and a substrate temperature of 200° C. The films are subsequently annealed at 600° C. for 30 minutes in air to form stoichiometric composition and to relieve the stress.

Positive photoresist patterns (Shipley 1350J, 1.5 μm) are used as etching masks for PZT and RuO₂ samples. These patterns can be removed by organic solvent after etching and etched steps were left on the sample surfaces. The step heights can be measured by a WYKO 3D surface profile meter. The etch rates can be determined by dividing the step heights by etching time. Meanwhile, the etch endpoint can also be observed directly.

The RIE system for PZT and RuO₂ etching may be one of those known in the art such as a SAMCO RIE-1C rf diode compact etcher with electrode separation of 5 cm and cathode area of 113 cm², which is shown schematically in FIG. 1. Both the cathode and etching samples are water cooled during the etching process.

Since the PZT solid solution consists of three components (PbO, ZrO₂ and TiO₂), the overall etch rate is dependent on the Zr/Ti ratio and the concentration of excess lead. This is because of the differing volatilities of the fluorides and chlorides of the constituent elements. Only the etch characteristics of PZT films with compositions close to the morphotrophic phase boundary were examined in the present invention. No substrate heating was used to avoid the loss of the lead from the masked areas which could result in degradation of the films at high temperatures. The etching was performed on water cooled substrate holders to avoid excessive heating from the plasma. The critical etch parameters studied were the gas pressure, RF power and the effect of O₂ addition to the CHClFCF₃ or CHCL₂CF₃ plasma. Since the objective is to etch the complete ferroelectric stack capacitor in a single run, the etch rate of RuO₂ was also studied under the same conditions as the PZT films. The range of the values of the parameters were chosen so as to observe the general trends in etching of these films with varying conditions. The parameter values were also limited by the stability of the plasma. FIG. 1 is a plot of the relative atomic concentration of Pb, Zr and Ti as a function of etch time. The concentrations of these elements were determined using the standard-less ratio method (more details regarding this method can be obtained from S. B. Desu and C. K. Kwok, Mat. Res. Soc. Symp. Proc., 200, 267 (1990)). This plot is a clear indication of the relative etch rates of the three components in the PZT solid solution. Initially, the relative atomic concentration of Zr and Ti decreases quite rapidly. The narrow scan results show that after the first 30 seconds of etching under these conditions, there is a continuous decrease in the Zr concentration while the relative Ti concentration appears to be nearly constant. It is evident from FIG. 7 that the etch rate of PbO is the limiting factor in the etching of PZT thin films and therefore any post-etch residues are primarily due to PbO.
The chlorides of Zr, Ti and Pb have higher vapor pressures compared to the corresponding fluorides at the etching temperature (~100° C.) and therefore it is expected that the primary volatile by-products will consist of the chlorides. However, the actual presence of these compounds in the by-products was not identified experimentally. The vapor pressure of the chlorides decreases in the order of TiCl₄ > ZrCl₄ > PbCl₂.

The effect of RF power on the etch rate of PZT films is shown in FIG. 6. In general, the etch rate increased with increasing RF power. It is well known that with an increase in the RF power, the sheath potential and the concentration of the reactive ions increase. The effect of gas pressure on the etch rate at different power values does suggest that the increase in etch rate with RF power is due to the increase in sheath potential.

What is claimed is:

1. A method of reactive ion etching a material that includes at least one of RuO₂ and lead zirconate titanate, comprising: placing the material into a chamber, the chamber containing at least one of CHCl₂CF₃ and CHCl₂CF₂, and producing a glow discharge in the chamber to etch the material.

2. The method of claim 1, wherein the material includes both RuO₂ and lead zirconate titanate.

3. The method of claim 2, wherein the glow discharge is produced by radio frequency.

4. The method of claim 3, wherein the radio frequency power is between 125 and 200 watts.

5. The method of claim 1, wherein the chamber includes O₂.

6. The method of claim 5, wherein the O₂ content in the chamber is between 10% and 50% of the total gas content in the chamber.

7. The method of claim 5, wherein the gas pressure in the chamber is less than about 175 mTorr.

8. A method of patterning a semiconductor device that includes at least one of RuO₂ and lead zirconate titanate, comprising: applying a mask over the material which covers a portion of the material and leaves exposes another portion of the material, placing the material with the applied mask into a chamber including at least one of CHCl₂CF₃ and CHCl₂CF₂, and producing a glow discharge in the chamber to reactivity ion etch the exposed portion of the material.

9. The method of claim 8, wherein the device includes both lead zirconate titanate and RuO₂, and the lead zirconate titanate functions as a dielectric and the RuO₂ functions as an electrode.

10. The method of claim 8, wherein the glow discharge is produced by radio frequency.

11. A semiconductor device, produced in accordance with the process of: applying at least one of lead zirconate titanate and RuSO₂ to a substrate, placing said substrate into a chamber, and reactive ion etching the at least one of said lead zirconate titanate and RuO₂ in an etching gas containing O₂ and at least one of CHCl₂CF₃ and CHCl₂CF₂.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,382,320
DATED : Jan. 17, 1995
INVENTOR(S) : Desu, et al.

It is certified that error appears in the above-indicated patent and that said Letters Patent is hereby corrected as shown below:

In Column 2, Line 22, change: "Ti_{1}O_{2}" to --TiO_{2}--.

In Column 2, Line 36, change: "see" to --see--.

In Column 4, Lines 30 & 31, change: "showed more smooth" to --is smoother--.

In Claim 8, Column 6, Line 12, change: "exposes" to --exposed--.

In Claim 11, Column 6, Line 25, change: "RuSO_{2}" to --RuO_{2}--.

In Claim 11, Column 6, Lines 26 & 27, change: "the at least one of" to --at least one of the--.

Signed and Sealed this Seventh Day of November, 1995

Attest:

BRUCE LEHMAN
Attesting Officer

Commissioner of Patents and Trademarks