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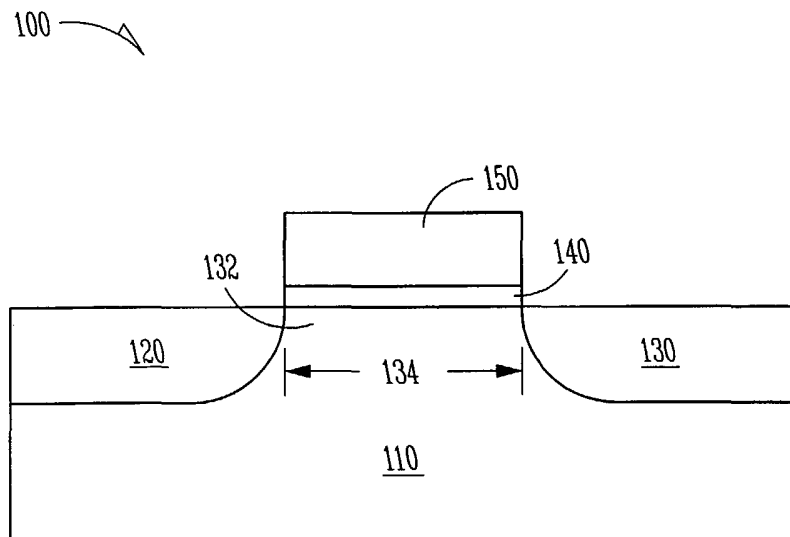
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(54) Title: HAFNIUM-ALUMINUM OXIDE DIELECTRIC FILMS



(57) **Abstract:** A dielectric film containing HfAlO₃ and a method of fabricating such a dielectric film produce a reliable gate dielectric having an equivalent oxide thickness thinner than attainable using SiO₂. A gate dielectric is formed by atomic layer deposition employing a hafnium sequence and an aluminum sequence. The hafnium sequence uses HfCl₄ and water vapor. The aluminum sequence uses either trimethylaluminum, A+(CH₃)₃, or DMEAA, an adduct of alane (AlH₃) and dimethylethylamine [N(CH₃)₂(C₂H₅)], with distilled water vapor. These gate dielectrics containing of HfAlO₃ film are thermodynamically stable such that the HfAlO₃ film will have minimal reactions with a silicon substrate or other structures during processing.



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HAFNIUM-ALUMINUM OXIDE DIELECTRIC FILMS

Related Applications

5 This application is related to the following, co-pending, commonly assigned

applications, incorporated herein by reference:

U.S. Application Serial No. 10/137,499, attorney docket no.

1303.050US1 entitled: "Atomic Layer-Deposited LaAlO₃ Films for Gate
10 Dielectrics,"

U.S. Application Serial No. 10/137,058, attorney docket no. 303.802US1
entitled: "Atomic Layer Deposition and Conversion,"

U.S. Application Serial No. 10/137,168, attorney docket no.
1303.048US1 entitled: "Atomic Layer of AlO_x for ULSI Gate Atomic Layer

15 Deposition for Gate Dielectric Layer," and

U.S. Application Serial No. 09/797,324, attorney docket no. 303.717US1
entitled: "Methods, Systems, and Apparatus for Uniform Chemical-Vapor
Depositions."

Field of the Invention

20 The invention relates to semiconductor devices and device fabrication. Specifically, the invention relates to gate dielectric layers of transistor devices and their method of fabrication.

Background of the Invention

25 The semiconductor device industry has a market driven need to improve speed performance, improve its low static (off-state) power requirements, and adapt to a wide range of power supply and output voltage requirements for it silicon based microelectronic products. In particular, in the fabrication of transistors, there is continuous pressure to reduce the size of devices such as transistors. The ultimate goal is to fabricate increasingly smaller and more
30 reliable integrated circuits (ICs) for use in products such as processor chips, mobile telephones, or memory devices such as DRAMs. The smaller devices are frequently powered by batteries, where there is also pressure to reduce the size of the batteries, and to extend the time between battery charges. This forces the

industry to not only design smaller transistors, but to design them to operate reliably with lower power supplies.

Currently, the semiconductor industry relies on the ability to reduce or scale the dimensions of its basic devices, primarily, the silicon based metal-oxide-semiconductor field effect transistor (MOSFET). A common
5 configuration of such a transistor is shown in Figure 1. While the following discussion uses Figure 1 to illustrate a transistor from the prior art, one skilled in the art will recognize that the present invention could be incorporated into the transistor shown in Figure 1 to form a novel transistor according to the invention.
10 The transistor 100 is fabricated in a substrate 110 that is typically silicon, but could be fabricated from other semiconductor materials as well. The transistor 100 has a first source/drain region 120 and a second source/drain region 130. A body region 132 is located between the first source/drain region and the second source/drain region, where the body region 132 defines a channel of the
15 transistor with a channel length 134. A gate dielectric, or gate oxide 140 is located on the body region 132 with a gate 150 located over the gate dielectric. Although the gate dielectric can be formed from materials other than oxides, the gate dielectric is typically an oxide, and is commonly referred to as a gate oxide. The gate may be fabricated from polycrystalline silicon (polysilicon), or other
20 conducting materials such as metal may be used.

In fabricating transistors to be smaller in size and reliably operating on lower power supplies, one important design criteria is the gate dielectric 140. The mainstay for forming the gate dielectric has been silicon dioxide, SiO_2 . A thermally grown amorphous SiO_2 layer provides an electrically and
25 thermodynamically stable material, where the interface of the SiO_2 layer with underlying Si provides a high quality interface as well as superior electrical isolation properties. In typical processing, use of SiO_2 on Si has provided defect charge densities on the order of $10^{10}/\text{cm}^2$, midgap interface state densities of approximately $10^{10}/\text{cm}^2$ eV, and breakdown voltages in the range of 15 MV/cm.
30 With such qualities, there would be no apparent need to use a material other than SiO_2 , but increased scaling and other requirements for gate dielectrics create the need to find other dielectric materials to be used for a gate dielectric.

What is needed is an alternate dielectric material for forming a gate dielectric that has a high dielectric constant relative to SiO_2 , and is thermodynamically stable with respect to silicon such that forming the dielectric on a silicon layer will not result in SiO_2 formation, or diffusion of material, such as dopants, into the gate dielectric from the underlying silicon layer.

Summary of the Invention

A solution to the problems as discussed above is addressed in embodiments according to the teachings of the present invention. In one embodiment, a method of forming a gate dielectric on a transistor body region includes the atomic layer deposition (ALD) of an amorphous film containing HfAlO_3 on the transistor body region. The ALD formation of the HfAlO_3 film is performed by pulsing a hafnium containing precursor into a reaction chamber containing a substrate, pulsing a first oxygen containing precursor into the reaction chamber, pulsing an aluminum containing precursor into the reaction chamber, and pulsing a second oxygen containing precursor into the reaction chamber. Each precursor is pulsed into the reaction chamber for a selected time period. A length of time for pulsing each precursor is selected according to the precursor used. Between each precursor pulsing, precursor excess and reaction by-products are removed from the reaction. The HfAlO_3 film thickness is controlled by repeating for a number of cycles the pulsing of the hafnium containing precursor, the first oxygen containing precursor, the aluminum containing precursor, and the second oxygen containing precursor until the desired thickness is formed.

Advantageously, a gate dielectric formed as a HfAlO_3 film has a larger dielectric constant than silicon dioxide, a relatively small leakage current, and good stability with respect to a silicon based substrate. Embodiments according to the teachings of the present invention include forming transistors, memory devices, and electronic systems having dielectric layers containing HfAlO_3 .

Other embodiments include structures for transistors, memory devices, and electronic systems with dielectric gates of HfAlO_3 film. Such dielectric gates provide a significantly thinner equivalent oxide thickness compared with a silicon oxide gate having the same physical thickness. Alternatively, such

dielectric gates provide a significantly thicker physical thickness than a silicon oxide gate having the same equivalent oxide thickness.

These and other embodiments, aspects, advantages, and features of the present invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art by reference to the following description of the invention and referenced drawings or by practice of the invention. The aspects, advantages, and features of the invention are realized and attained by means of the instrumentalities, procedures, and combinations particularly pointed out in the appended claims.

10 Brief Description of the Drawings

Figure 1 depicts a common configuration of a transistor.

Figure 2A depicts an embodiment of an atomic layer deposition system for processing a HfAlO_3 film according to the teachings of the present invention.

Figure 2B depicts an embodiment of a gas-distribution fixture of an atomic layer deposition chamber for processing a HfAlO_3 film according to the teachings of the present invention.

Figure 3 illustrates a flow diagram of elements for an embodiment of a method to process a HfAlO_3 film according to the teachings of the present invention.

20 Figure 4 depicts an embodiment of a configuration of a transistor capable of being fabricated according to the teachings of the present invention.

Figure 5 illustrates a perspective view of an embodiment of a personal computer incorporating devices according to the teachings of the present invention.

25 Figure 6 illustrates a schematic view of an embodiment of a central processing unit incorporating devices according to the teachings of the present invention.

Figure 7 illustrates a schematic view of an embodiment of a DRAM memory device according to the teachings of the present invention.

Detailed Description of the Preferred Embodiments

In the following detailed description of the invention, reference is made to the accompanying drawings which form a part hereof, and in which is shown, by way of illustration, specific embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the present invention.

The terms wafer and substrate used in the following description include any structure having an exposed surface with which to form the integrated circuit (IC) structure of the invention. The term substrate is understood to include semiconductor wafers. The term substrate is also used to refer to semiconductor structures during processing, and may include other layers that have been fabricated thereupon. Both wafer and substrate include doped and undoped semiconductors, epitaxial semiconductor layers supported by a base semiconductor or insulator, as well as other semiconductor structures well known to one skilled in the art. The term conductor is understood to include semiconductors, and the term insulator or dielectric is defined to include any material that is less electrically conductive than the materials referred to as conductors.

The term "horizontal" as used in this application is defined as a plane parallel to the conventional plane or surface of a wafer or substrate, regardless of the orientation of the wafer or substrate. The term "vertical" refers to a direction perpendicular to the horizontal as defined above. Prepositions, such as "on", "side" (as in "sidewall"), "higher", "lower", "over" and "under" are defined with respect to the conventional plane or surface being on the top surface of the wafer or substrate, regardless of the orientation of the wafer or substrate. The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is defined only by the appended claims, along with the full scope of equivalents to which such claims are entitled.

A gate dielectric 140 of Figure 1, when operating in a transistor, has both a physical gate dielectric thickness and an equivalent oxide thickness (t_{eq}). The

equivalent oxide thickness quantifies the electrical properties, such as capacitance, of a gate dielectric 140 in terms of a representative physical thickness. t_{eq} is defined as the thickness of a theoretical SiO_2 layer that would be required to have the same capacitance density as a given dielectric, ignoring

5 leakage current and reliability considerations.

A SiO_2 layer of thickness, t , deposited on a Si surface as a gate dielectric will also have a t_{eq} larger than its thickness, t . This t_{eq} results from the capacitance in the surface channel on which the SiO_2 is deposited due to the formation of a depletion/inversion region. This depletion/inversion region can
10 result in t_{eq} being from 3 to 6 Angstroms ($\text{\AA}$) larger than the SiO_2 thickness, t . Thus, with the semiconductor industry driving to someday scale the gate dielectric equivalent oxide thickness to under 10 $\text{\AA}$, the physical thickness requirement for a SiO_2 layer used for a gate dielectric would be need to be approximately 4 to 7 $\text{\AA}$.

15 Additional requirements on a SiO_2 layer would depend on the gate electrode used in conjunction with the SiO_2 gate dielectric. Using a conventional polysilicon gate would result in an additional increase in t_{eq} for the SiO_2 layer. This additional thickness could be eliminated by using a metal gate electrode, though metal gates are not currently used in complementary metal-oxide-
20 semiconductor field effect transistor (CMOS) technology. Thus, future devices would be designed towards a physical SiO_2 gate dielectric layer of about 5 $\text{\AA}$ or less. Such a small thickness requirement for a SiO_2 oxide layer creates additional problems.

Silicon dioxide is used as a gate dielectric, in part, due to its electrical
25 isolation properties in a SiO_2 - Si based structure. This electrical isolation is due to the relatively large band gap of SiO_2 (8.9 eV) making it a good insulator from electrical conduction. Signification reductions in its band gap would eliminate it as a material for a gate dielectric. As the thickness of a SiO_2 layer decreases, the number of atomic layers, or monolayers of the material in the thickness
30 decreases. At a certain thickness, the number of monolayers will be sufficiently small that the SiO_2 layer will not have a complete arrangement of atoms as in a larger or bulk layer. As a result of incomplete formation relative to a bulk

structure, a thin SiO₂ layer of only one or two monolayers will not form a full band gap. The lack of a full band gap in a SiO₂ gate dielectric would cause an effective short between an underlying Si channel and an overlying polysilicon gate. This undesirable property sets a limit on the physical thickness to which a SiO₂ layer can be scaled. The minimum thickness due to this monolayer effect is thought to be about 7-8 Å. Therefore, for future devices to have a t_{eq} less than about 10 Å, other dielectrics than SiO₂ need to be considered for use as a gate dielectric.

For a typical dielectric layer used as a gate dielectric, the capacitance is determined as one for a parallel plate capacitance: $C = \kappa \epsilon_0 A / t$, where κ is the dielectric constant, ϵ_0 is the permittivity of free space, A is the area of the capacitor, and t is the thickness of the dielectric. The thickness, t , of a material is related to t_{eq} for a given capacitance with the dielectric constant of SiO₂, $\kappa_{ox} = 3.9$, associated with t_{eq} , as

$$t = (\kappa / \kappa_{ox}) t_{eq} = (\kappa / 3.9) t_{eq}.$$

Thus, materials with a dielectric constant greater than that of SiO₂, 3.9, will have a physical thickness that can be considerably larger than a desired t_{eq} , while providing the desired equivalent oxide thickness. For example, an alternate dielectric material with a dielectric constant of 10 could have a thickness of about 25.6 Å to provide a t_{eq} of 10 Å, not including any depletion/inversion layer effects. Thus, the reduced equivalent oxide thickness of transistors can be realized by using dielectric materials with higher dielectric constants than SiO₂.

The thinner equivalent oxide thickness required for lower transistor operating voltages and smaller transistor dimensions may be realized by a significant number of materials, but additional fabricating requirements makes determining a suitable replacement for SiO₂ difficult. The current view for the microelectronics industry is still for Si based devices. This requires that the gate dielectric employed be grown on a silicon substrate or silicon layer, which places significant restraints on the substitute dielectric material. During the formation of the dielectric on the silicon layer, there exists the possibility that a small layer of SiO₂ could be formed in addition to the desired dielectric. The result would effectively be a dielectric layer consisting of two sublayers in parallel with each

other and the silicon layer on which the dielectric is formed. In such a case, the resulting capacitance would be that of two dielectrics in series. As a result, the t_{eq} of the dielectric layer would be the sum of the SiO_2 thickness and a multiplicative factor of the thickness of the dielectric being formed, written as

5
$$t_{eq} = t_{\text{SiO}_2} + (\kappa_{ox} / \kappa)t.$$

Thus, if a SiO_2 layer is formed in the process, the t_{eq} is again limited by a SiO_2 layer. In the event that a barrier layer is formed between the silicon layer and the desired dielectric in which the barrier layer prevents the formation of a SiO_2 layer, the t_{eq} would be limited by the layer with the lowest dielectric constant.

10 However, whether a single dielectric layer with a high dielectric constant or a barrier layer with a higher dielectric constant than SiO_2 is employed, the layer interfacing with the silicon layer must provide a high quality interface to maintain a high channel carrier mobility.

In a recent article by G. D. Wilk et al., Journal of Applied Physics, vol. 89: no. 10, pp. 5243-5275 (2001), material properties of high dielectric materials for gate dielectrics were discussed. Among the information disclosed was the viability of Al_2O_3 as a substitute for SiO_2 . Al_2O_3 was disclosed as having favourable properties for use as a gate dielectric such as high band gap, thermodynamic stability on Si up to high temperatures, and an amorphous
20 structure. In addition, Wilk disclosed that forming a layer of Al_2O_3 on silicon does not result in a SiO_2 interfacial layer. However, the dielectric constant of Al_2O_3 is only 9, where thin layers may have a dielectric constant of about 8 to about 10. Though the dielectric constant of Al_2O_3 is in an improvement over

SiO₂, a higher dielectric constant for a gate dielectric is desirable. Other dielectrics and their properties discussed by Wilk include

Material	Dielectric Constant (κ)	Band gap E _g (eV)	Crystal Structure(s)
SiO ₂	3.9	8.9	Amorphous
Si ₃ N ₄	7	5.1	Amorphous
Al ₂ O ₃	9	8.7	Amorphous
Y ₂ O ₃	15	5.6	Cubic
La ₂ O ₃	30	4.3	Hexagonal, Cubic
Ta ₂ O ₅	26	4.5	Orthorhombic
TiO ₂	80	3.5	Tetrag. (rutile, anatase)
HfO ₂	25	5.7	Mono., Tetrag., Cubic
ZrO ₂	25	7.8	Mono., Tetrag., Cubic

One of the advantages using SiO₂ as a gate dielectric has been that the formation of the SiO₂ layer results in an amorphous gate dielectric. Having an amorphous structure for a gate dielectric is advantageous because grain boundaries in polycrystalline gate dielectrics provide high leakage paths. Additionally, grain size and orientation changes throughout a polycrystalline gate dielectric can cause variations in the film's dielectric constant. The abovementioned material properties including structure are for the materials in a bulk form. The materials having the advantage of a high dielectric constants relative to SiO₂ also have the disadvantage of a crystalline form, at least in a bulk configuration. The best candidates for replacing SiO₂ as a gate dielectric are those with high dielectric constant, which can be fabricated as a thin layer with an amorphous form.

In co-pending, commonly assigned U.S. patent applications: entitled "Atomic Layer-Deposited LaAlO₃ Films for Gate Dielectrics," attorney docket no. 1303.050US1, serial number 10/137,499, LaAlO₃ is disclosed as a

replacement for SiO₂ for forming gate dielectrics and other dielectric films in electronic devices such as MOS transistors. This application discloses, among other things, forming layers of LaAlO₃ on silicon by atomic layer deposition using a lanthanum containing source and an aluminum containing source.

- 5 Controlling a lanthanum sequence deposition and an aluminum sequence deposition allows for the formation of a gate dielectric having a composition with a predetermined dielectric constant.

 In an embodiment according to the teachings of the present invention, layers of HfAlO₃ are deposited on silicon using atomic layer deposition (ALD),
10 also known as atomic layer epitaxy (ALE). ALD was developed in the early 1970's as a modification of chemical vapor deposition (CVD) and is also called "alternatively pulsed-CVD." In ALD, gaseous precursors are introduced one at a time to the substrate surface mounted within a reaction chamber (or reactor). This introduction of the gaseous precursors takes the form of pulses of each
15 gaseous precursor. Between the pulses, the reaction chamber is purged with an inert gas or evacuated. In the first pulsing phase, reaction with the substrate occurs with the precursor saturatively chemisorbed at the substrate surface. Subsequent purging with an inert gas removes precursor excess from the reaction chamber.

20 The second pulsing phase introduces another precursor on the substrate where the growth reaction of the desired film takes place. Subsequent to the film growth reaction, reaction byproducts and precursor excess are purged from the reaction chamber. With favourable precursor chemistry where the precursors adsorb and react with each other on the substrate aggressively, one ALD cycle
25 can be preformed in less than one second in properly designed flow type reaction chambers. Typically, precursor pulse times range from about 0.5 sec to about 2 to 3 seconds.

 Advantageously, in ALD, the saturation of all the reaction and purging phases makes the growth self-limiting. This self-limiting growth results in large
30 area uniformity and conformality, which has important applications for such cases as planar substrates, deep trenches, and in the processing of porous silicon and high surface area silica and alumina powders. Significantly, ALD provides

for controlling film thickness in a straightforward, simple manner by controlling the number of growth cycles.

ALD was originally developed to manufacture luminescent and dielectric films needed in electroluminescent displays. Significant efforts have been made to apply ALD to the growth of doped zinc sulfide and alkaline earth metal sulfide films. Additionally, ALD has been studied for the growth of different epitaxial II-V and II-VI films, nonepitaxial crystalline or amorphous oxide and nitride films and multilayer structures of these. There also has been considerable interest towards the ALD growth of silicon and germanium films, but due to the difficult precursor chemistry, this has not been very successful.

The precursors may be gaseous, liquid or solid. However, liquid or solid precursors must be volatile. The vapor pressure must be high enough for effective mass transportation. Also, solid and some liquid precursors need to be heated inside the reaction chamber and introduced through heated tubes to the substrates. The necessary vapor pressure must be reached at a temperature below the substrate temperature to avoid the condensation of the precursors on the substrate. Due to the self-limiting growth mechanisms of ALD, relatively low vapor pressure solid precursors can be used though evaporation rates may somewhat vary during the process because of changes in their surface area.

There are several other requirements for precursors used in ALD. The precursors must be thermally stable at the substrate temperature because their decomposition would destroy the surface control and accordingly the advantages of the ALD method which relies on the reactant of the precursor at the substrate surface. Of course, a slight decomposition, if slow compared to the ALD growth, can be tolerated.

The precursors have to chemisorb on or react with the surface, though the interaction between the precursor and the surface as well as the mechanism for the adsorption is different for different precursors. The molecules at the substrate surface must react aggressively with the second precursor to form the desired solid film. Additionally, precursors should not react with the film to cause etching, and precursors should not dissolve in the film. Using highly

reactive precursors in ALD contrasts with the selection of precursors for conventional CVD.

The by-products in the reaction must be gaseous in order to allow their easy removal from the reaction chamber. Further, the by-products should not
5 react or adsorb on the surface.

In one embodiment, a HfAlO_3 film is formed on a substrate mounted in a reaction chamber by pulsing a hafnium containing precursor into the reaction chamber followed by pulsing a first oxygen containing precursor, and by pulsing an aluminum containing precursor into the reaction chamber followed by pulsing
10 a second oxygen containing precursor into the reaction chamber. Between each pulsing, a purging gas is introduced into the reaction chamber. Pulsing a hafnium containing precursor into the reaction chamber followed by pulsing a first oxygen containing precursor with subsequent purging after each pulsing constitutes a hafnium sequence. Similarly, pulsing an aluminum containing
15 precursor into the reaction chamber followed by pulsing a second oxygen containing precursor into the reaction chamber with subsequent purging after each pulsing constitutes an aluminum sequence. The selection of the first oxygen containing precursor depends upon the hafnium containing precursor pulsed into the chamber, and likewise, the second oxygen containing precursor
20 depends upon the aluminum precursor pulsed into the chamber. Additionally, different purging gases can be employed for the hafnium sequence and the aluminum sequence. Furthermore, pulsing each precursor into the reaction chamber is individually controlled for a predetermined period, where the predetermined period for each precursor differs according to the nature of the
25 precursor.

The precursors are selected such that performing one hafnium sequence followed by performing an aluminum sequence completes one cycle of ALD deposition of a HfAlO_3 layer. The thickness of this HfAlO_3 layer will depend on the precursors used, the period of the pluses, and the processing temperature. A
30 HfAlO_3 film with a predetermined thickness is formed by repeating for a number of cycles the hafnium sequence and the aluminum sequence. Once a HfAlO_3 film with the desired thickness is formed, the HfAlO_3 film is annealed.

In an embodiment of the present invention, precursor gases are used to form HfAlO_3 films as a gate dielectric on a transistor body. Alternately, solid or liquid precursors can be used in an appropriately designed reaction chamber.

ALD formation of other materials is disclosed in co-pending, commonly

5 assigned U.S. patent application: entitled "Atomic Layer Deposition and Conversion," attorney docket no. 303.802US1, serial number 10/137,058, and "Atomic Layer of AlO_x for ULSI Gate Atomic Layer Deposition for Gate Dielectric Layer," attorney docket no. 1303.048US1, serial number 10/137,168.

Figure 2A depicts an embodiment of an atomic layer deposition system
10 for processing a HfAlO_3 film according to the teachings of the present invention. The elements depicted are those elements necessary for discussion of the present invention such that those skilled in the art may practice the present invention without undue experimentation. A further discussion of the ALD reaction chamber can be found in co-pending, commonly assigned U.S. patent
15 application: entitled "Methods, Systems, and Apparatus for Uniform Chemical-Vapor Depositions," attorney docket no. 303.717US1, serial number 09/797,324, incorporated herein by reference. In Figure 2A, a substrate 210 is placed inside a reaction chamber 220 of ALD system 200. Also located within the reaction chamber 220 is a heating element 230 which is thermally coupled to substrate
20 210 to control the substrate temperature. A gas-distribution fixture 240 introduces precursor gases to the substrate 210. Each precursor gas originates from individual gas sources 251- 254 whose flow is controlled by mass-flow controllers 256- 259, respectively. The gas sources 251-254 provide a precursor gas either by storing the precursor as a gas or by providing a location and
25 apparatus for evaporating a solid or liquid material to form the selected precursor gas.

Also included in the ALD system are purging gas sources 261, 262, each of which is coupled to mass-flow controllers 266, 267, respectively. The gas sources 251-254 and the purging gas sources 261-262 are coupled by their
30 associated mass-flow controllers to a common gas line or conduit 270 which is coupled to the gas-distribution fixture 240 inside the reaction chamber 220. Gas conduit 270 is also coupled to vacuum pump, or exhaust pump, 281 by mass-

flow controller 286 to remove excess precursor gases, purging gases, and by-product gases at the end of a purging sequence from the gas conduit.

Vacuum pump, or exhaust pump, 282 is coupled by mass-flow controller 287 to remove excess precursor gases, purging gases, and by-product gases at the
5 end of a purging sequence from the reaction chamber 220. For convenience, control displays, mounting apparatus, temperature sensing devices, substrate maneuvering apparatus, and necessary electrical connections as are known to those skilled in the art are not shown in Figure 2A.

Figure 2B depicts an embodiment of a gas-distribution fixture of an
10 atomic layer deposition chamber for processing a HfAlO_3 film according to the teachings of the present invention. Gas-distribution fixture 240 includes a gas-distribution member 242, and a gas inlet 244. Gas inlet 244 couples the gas-distribution member 242 to the gas conduit 270 of Figure 2A. Gas-distribution member 242 includes gas-distribution holes, or orifices, 246 and gas-distribution
15 channels 248. In the exemplary embodiment, holes 246 are substantially circular with a common diameter in the range of 15-20 microns; gas-distribution channels 248 have a common width in the range of 20-45 microns. The surface 249 of the gas distribution member having gas-distribution holes 246 is substantially planar and parallel to the substrate 210 of Figure 2A. However,
20 other embodiments use other surface forms as well as shapes and sizes of holes and channels. The distribution and size of holes may also affect deposition thickness and thus might be used to assist thickness control. Holes 246 are coupled through gas-distribution channels 248 to gas inlet 244. Though the ALD system 200 is well suited for practicing the present invention, other ALD
25 systems commercially available can be used.

The use, construction and fundamental operation of reaction chambers for deposition of films are understood by those of ordinary skill in the art of semiconductor fabrication. The present invention can be practiced on a variety of such reaction chambers without undue experimentation. Furthermore, one of
30 ordinary skill in the art will comprehend the necessary detection, measurement, and control techniques in the art of semiconductor fabrication upon reading the disclosure.

Figure 3 illustrates a flow diagram of elements for an embodiment of a method to process a HfAlO_3 film according to the teachings of the present invention. The method can be implemented with the atomic layer deposition system of Figure 2A,B. At block 305, a substrate is prepared. The substrate
5 used for forming a transistor is typically a silicon or silicon containing material. In other embodiments, germanium, gallium arsenide, and silicon-on-sapphire substrates may be used. This preparation process includes cleaning of the substrate 210 and forming layers and regions of the substrate, such as drains and sources of a metal oxide semiconductor (MOS) transistor, prior to forming a gate
10 dielectric. The sequencing of the formation of the regions of the transistor being processed follows typical sequencing that is generally performed in the fabrication of a MOS transistor as is well known to those skilled in the art. Included in the processing prior to forming a gate dielectric is the masking of substrate regions to be protected during the gate dielectric formation, as is
15 typically performed in MOS fabrication. In this embodiment, the unmasked region includes a body region of a transistor, however one skilled in the art will recognize that other semiconductor device structures may utilize this process. Additionally, the substrate 210 in its ready for processing form is conveyed into a position in reaction chamber 220 for ALD processing.

20 At block 310, a precursor containing hafnium is pulsed into reaction chamber 220. In particular, HfCl_4 is used as a source material. The HfCl_4 is pulsed into reaction chamber 220 through the gas-distribution fixture 240 onto substrate 210. The flow of the HfCl_4 is controlled by mass-flow controller 256 from gas source 251. The HfCl_4 source gas temperature ranges from about 130
25 °C at about 154 °C. The HfCl_4 reacts with the surface of the substrate 210 in the desired region defined by the unmasked areas of the substrate 210.

At block 315, a first purging gas is pulsed into the reaction chamber 220. In particular, pure nitrogen with a purity greater than 99.99% is used as a purging gas for HfCl_4 . The nitrogen flow is controlled by mass-flow controller 266 from
30 the purging gas source 261 into the gas conduit 270. Using the pure nitrogen purge avoids overlap of the precursor pulses and possible gas phase reactions. Following the purge, at block 320, a first oxygen containing precursor is pulsed

into the reaction chamber 220. For the hafnium sequence using HfCl_4 as the precursor, water vapor is selected as the precursor acting as an oxidizing reactant to form a hafnium oxide on the substrate 210. The water vapor is pulsed into the reaction chamber 220 through gas conduit 270 from gas source 252 by mass-flow controller 257 with a flow rate ranging from about 0.5 to about 1.0 mPa m³/sec. The water vapor aggressively reacts at the surface of substrate 210.

Following the pulsing of oxidizing reactant water vapor, at block 325, the first purging gas is injected into the reaction chamber 220. In the HfCl_4 / water vapor sequence, pure nitrogen gas is used to purge the reaction chamber after pulsing each precursor gas. Excess precursor gas, and reaction by-products are removed from the system by the purge gas in conjunction with the exhausting of the reaction chamber 220 using vacuum pump 282 through mass-flow controller 287, and exhausting of the gas conduit 270 by the vacuum pump 281 through mass-flow controller 286.

During the HfCl_4 / water vapor sequence, the substrate is held between about 350 °C and about 550 °C by the heating element 230 with the reaction chamber used in a low -pressure (250 Pa) hot wall configuration. In other embodiments the substrate is held between about 500 °C and 1000 °C. The HfCl_4 pulse time ranges from about 1.0 sec to about 2.0 sec. After the HfCl_4 pulse, the hafnium sequence continues with a purge pulse followed by a water vapor pulse followed by a purge pulse. In one embodiment, performing a purge pulse followed by a water vapor pulse followed by a purge pulse takes about 2 seconds. In another embodiment, each pulse in the hafnium sequence after the HfCl_4 pulse has a 2 second pulse period.

At block 330, a precursor containing aluminum is pulsed into the reaction chamber 220. In one embodiment, trimethylaluminium (TMA), $\text{Al}(\text{CH}_3)_3$, is used as the aluminum containing precursor following the HfCl_4 / ozone sequence. The TMA is pulsed to the surface of the substrate 210 through gas-distribution fixture 240 from gas source 253 by mass-flow controller 258. The TMA is introduced onto the hafnium oxide film that was formed during the HfCl_4 / water vapor sequence.

At block 335, a second purging gas is introduced into the system. For a TMA precursor, purified argon is used as a purging and carrier gas. The argon flow is controlled by mass-flow controller 267 from the purging gas source 262 into the gas conduit 270 and subsequently into the reaction chamber 220.

- 5 Following the argon purge, at block 340, a second oxygen containing precursor is pulsed into the reaction chamber 220. For the aluminum sequence using TMA as the precursor, distilled water vapor is selected as the precursor acting as an oxidizing reactant to interact with the TMA on the substrate 210. The distilled water vapor is pulsed into the reaction chamber 220 through gas conduit 270
- 10 from gas source 254 by mass-flow controller 259. The distilled water vapor aggressively reacts at the surface of substrate 210 to form a HfAlO_3 film.

- Following the pulsing of the distilled water vapor acting as an oxidizing reactant, at block 345, the second purging gas is injected into the reaction chamber 200. In the TMA / distilled water vapor sequence, argon gas is used to
- 15 purge the reaction chamber after pulsing each precursor gas. In another embodiment, pure nitrogen is again used as the purging gas. Excess precursor gas, and reaction by-products are removed from the system by the purge gas in conjunction with the exhausting of the reaction chamber 220 using vacuum pump 282 through mass-flow controller 287, and exhausting of the gas conduit
- 20 270 by the vacuum pump 281 through mass-flow controller 286. This completes not only the TMA/distilled water vapor sequence, but it also completes a hafnium sequence / aluminum sequence cycle forming a HfAlO_3 layer having a set thickness associated with one ALD cycle.

- During the TMA / distilled water vapor sequence, the substrate is held
- 25 between about 350 °C and about 450 °C by the heating element 230. The reaction chamber is maintained at about 150 °C to minimize reactant condensation. The process pressure is maintained at about 230 mTorr during the pulsing of the precursor gases and at about 200 mTorr for the purging gases. Pulse times for the TMA and the distilled water vapor were about 1 sec for both
- 30 precursors, with purging pulse times of about 15 secs. In one embodiment, the substrate temperature is maintained at about 350 °C for the complete HfCl_4 / water vapor / TMA / distilled water vapor cycle. In another embodiment, the

substrate temperature is maintained at about 550 °C for the complete HfCl_4 / water vapor / TMA / distilled water vapor cycle.

As an alternate aluminum sequence, a DMEAA/oxygen sequence can be employed rather than the TMA / distilled water vapor sequence. The aluminum
5 containing precursor DMEAA is an adduct of alane (AlH_3) and dimethylethylamine [$\text{N}(\text{CH}_3)_2(\text{C}_2\text{H}_5)$]. At block 330, the DMEAA is pulsed to the substrate 210 surface from gas source 253. The DMEAA gas can be provided to gas source 253 through a bubbler-type evaporation controlled at 25 °C. The purging and carrier gas associated with DMEAA, at block 335, is
10 hydrogen from purging gas source 262. At block 340, to provide the necessary reaction at the substrate 210, oxygen as the second oxygen containing precursor is pulsed into the reaction chamber 220 from gas source 254. At block 345, hydrogen purging gas is again flowed through the reaction chamber 220 from purging gas source 262.

15 During the DMEAA/oxygen sequence, the substrate is held between about 100°C and about 125 °C by the heating element 230. The process pressure during the DMEAA/oxygen sequence is maintained at about 30 mTorr.

In an alternate aluminum sequence using DMEAA, a DMEAA/ distilled water vapor sequence can be used under the same temperature and pressure ranges
20 as the TMA / distilled water sequence. In an embodiment of the present invention, the substrate temperature is maintained at about 350 °C for the complete HfCl_4 / water vapor / DMEAA / distilled water vapor cycle. Alternately, the complete HfCl_4 / water vapor / DMEAA / distilled water vapor cycle can be performed with the substrate temperature maintained at about 550
25 °C.

The thickness of a HfAlO_3 film after one cycle is determined by the pulsing periods used in the hafnium sequence and the aluminum sequence at a given temperature. The pulsing periods of the ALD process depend upon the characteristics of the reaction system 200 employed and the precursor and
30 purging sources. Typically, at a given temperature, the pulsing periods can vary over a significant range above some minimum pulse time for the precursors, without substantially altering the growth rate. Once a set of periods for one cycle

is determined, the growth rate for the HfAlO_3 film will be set at a value such as N nm/cycle. For a desired HfAlO_3 film thickness, t , in an application such as forming a gate dielectric of a MOS transistor, the ALD process should be repeated for t/N cycles.

- 5 At block 350, it is determined whether the HfAlO_3 film is of the desired thickness, t . As mentioned, the desired thickness should be completed after t/N cycles. If less than t/N cycles have been completed, the process starts over at block 310 with the pulsing of the precursor containing hafnium, which in the embodiment discussed above is a HfCl_4 gas. If t/N cycles have completed, no further ALD processing is required and the HfAlO_3 film, at block 355, is annealed. The annealing is a final heating cycle for producing the HfAlO_3 film and is performed at a temperature between about 300°C and about 800°C to produce optimum performance as a dielectric insulator. The annealing can be performed in an inert or nitrogen atmosphere.
- 10 At block 360, after forming the HfAlO_3 film, processing the device containing the HfAlO_3 film is completed. In one embodiment, completing the device includes completing the formation of a transistor. Alternately, completing the process includes completing the construction of a memory device having an array with access transistors formed with HfAlO_3 film gate dielectrics.
- 15 Further, in another embodiment, completing the process includes the formation of an electronic system including an information handling device that uses electronic devices with transistors formed with HfAlO_3 film gate dielectrics. Typically, information handling devices such as computers include many memory devices, having many access transistors.
- 20 In one embodiment, a HfAlO_3 film for use as a gate dielectric is formed on a body region of a transistor by the ALD process using a hafnium/water vapor/aluminum/water vapor cycle. This cycle is the combination of a hafnium/water vapor sequence and an aluminum/water sequence. Terminating the cycle at the end of a hafnium/water vapor sequence would typically result in a HfO_2 film. Performing just an aluminum/water sequence would typically result in an Al_2O_3 film.
- 25
- 30

In a recent article by W. Zhu et al., International Electron Devices Meeting 01, pp. 463- 466 (2001), growth of HfO_2 and HfAlO films by the Jet-Vapor deposition method was reported. HfO_2 films of approximately 3 nm appear to crystallize at 400 °C - 500 °C, while HfAlO films with about 6.8% Al crystallize at about 200 °C higher, and HfAlO films with about 31.7% Al crystallize at about 400 °C higher than the HfO_2 films. Thus, this article indicates that HfAlO films tend to form crystalline structures when processed at higher temperatures. However, amorphous structures have advantages as gate dielectrics.

10 In a recent article by J. Aarik et al., Applied Surface Science, vol. 173, pp. 15-21 (2001), growth of HfO_2 films by ALD using a HfCl_4 / water vapor sequence was reported. The HfCl_4 source temperature ranged from 130 °C to 154 °C with the substrate temperature maintained at different temperatures in the range from 500 °C to 1000 °C. For a substrate temperature of 940 °C and a
15 water vapor flow rate of 0.7 mPa /m³, the resultant film structure was found to be dependant on the HfCl_4 source temperature. At a HfCl_4 source temperature of 128 °C the film was monoclinic with a growth rate of 0.034 nm/cycle, while at a HfCl_4 source temperature of 152 °C the film was cubic with a growth rate of 0.067 nm/cycle. The report concluded the surface structure of HfO_2 films grown
20 by ALD using HfCl_4 and water vapor can be varied when changing the growth temperature and precursor doses.

In a recent article by Y. Kim et al., Applied Physics Letters, vol. 71 (25), pp. 3604 - 3606 (1997), growth of Al_2O_3 films by ALD using a TMA / distilled water vapor sequence was reported. With the substrate temperature maintained
25 at 370 °C, and the pulsing time for the TMA and the distilled water vapor set each at 1 second, the growth rate for the Al_2O_3 films was determined to be about 0.19 nm per cycle. This growth rate was determined to be the same for TiN, Si, and SiO_2 substrates. An Al_2O_3 growth rate of 24.4 Å per cycle at 100 °C by ALD, for a cycle using DMEAA as a precursor for five Al depositions followed
30 by O_2 plasma oxidation, was reported in a recent article by C. Jeong et al., Japanese Journal of Applied Physics, vol. 40 part 1 no. 1, pp. 285 - 289 (2001). Typically, Al_2O_3 films formed by ALD are amorphous.

A dielectric film containing HfAlO_3 , Al_2O_3 , and HfO_2 has a dielectric constant ranging from the dielectric constant of Al_2O_3 , 9, to the dielectric constant of HfO_2 , 25. By controlling the number of cycles of the hafnium sequence and the number of cycles of the aluminum sequence, the amount of hafnium and aluminum deposited on the surface region of a substrate can be controlled. Thus, a dielectric film formed by ALD using a hafnium sequence and a aluminum sequence can be formed with a composition containing selected or predetermined percentages of HfAlO_3 , Al_2O_3 , and HfO_2 , in which case the effective dielectric constant of the film will be selected or predetermined in the range from 9 to 25. Furthermore, using an aluminum sequence subsequent to a hafnium sequence, the resulting dielectric containing HfAlO_3 should be amorphous.

In addition to separately controlling the number of cycles of the hafnium sequence and the aluminum sequence in the ALD process, a dielectric film containing HfAlO_3 can be engineered with selected characteristics by also controlling precursor materials for each sequence, processing temperatures and pressures for each sequence, individual precursor pulsing times, and heat treatment at the end of the process, at the end of each cycle, and at the end of each sequence. The heat treatment may include in situ annealing in various atmospheres including argon and nitrogen.

The pulsing times for precursors range from about 0.5 sec to about 2 to 3 sec, though longer pulses can be employed. Typically, pulsing times for purging gases will range from a time equal to its associated precursor pulse time to an order of magnitude larger than the associated precursor pulse time in order than all excess material and by-products be purged from the reaction system. Generally, the pulsing times for purging gases will range from about one sec to about 30 seconds. In one embodiment, the pulsing times for purging gases is in the 1- 2 sec range.

The growth rates for an engineered film containing HfAlO_3 will be controlled by the growth rates of the individual sequences and typically can be from about .34 Å per cycle to about 5 Å per cycle. Other growth rates may also be attained.

A range of equivalent oxide thickness, t_{eq} , attainable in various embodiments of the present invention is associated with the capability to provide a composition having a dielectric constant in the range from about 9 to about 25, and the capability to attain physical film thickness in the range of from about 2 to about 3 nm and above. The t_{eq} range in accordance with the present invention are shown in the following

	Physical Thickness $t = 0.5 \text{ nm } (5 \text{ \AA})$	Physical Thickness $t = 1.0 \text{ nm } (10 \text{ \AA})$	Physical Thickness $t = 5.0 \text{ nm } (50 \text{ \AA})$
κ	$t_{eq} (\text{\AA})$	$t_{eq} (\text{\AA})$	$t_{eq} (\text{\AA})$
9	2.17	4.33	21.67
17	1.15	2.29	11.47
21	.93	1.86	9.29
25	.78	1.56	7.8

The lower limit on the scaling of a layer containing HfAlO_3 would depend on the monolayers of the film necessary to develop a full band gap such that good insulation is maintained between an underlying silicon layer and an overlying conductive layer to the HfAlO_3 film. This requirement is necessary to avoid possible short circuit effects between the underlying silicon layer and the overlying conductive layer. From above, it is apparent that a film containing HfAlO_3 can be attained with a t_{eq} ranging from 3 $\text{\AA}$ to 12 $\text{\AA}$. Further, a film with essentially no interfacial layer can provide a t_{eq} significantly less than 2 or 3 $\text{\AA}$, even less than 1.5 $\text{\AA}$.

The novel process described above provides significant advantages by performing atomic layer deposition with a hafnium sequence/ aluminum sequence deposition cycle. Further, by independently controlling the various parameters for each sequence a gate dielectric with a selected dielectric constant can be formed. Additionally, the novel process can be implemented to form transistors, memory devices, and information handling devices.

A transistor 100 as depicted in Figure 1 can be formed by forming a source/drain region 120 and another source/drain region 130 in a silicon based substrate 110 where the two source/drain regions 120, 130 are separated by a body region 132. The body region 132 separated by the source/drain 120 and the source/drain 130 defines a channel having a channel length 134. A HfAlO_3 film is formed by ALD by pulsing a hafnium containing precursor into a reaction chamber containing the substrate 110, pulsing a first oxygen containing precursor into the reaction chamber, pulsing an aluminum containing precursor into the reaction chamber, and pulsing a second oxygen containing precursor into the reaction chamber. Each precursor is pulsed into the reaction chamber for a selected time period. A length of time for pulsing each precursor is selected according to the precursor used. Between each precursor pulsing, precursor excess and reaction by-products are removed from the reaction chamber. The HfAlO_3 film thickness is controlled by repeating for a number of cycles the pulsing of the hafnium containing precursor, the first oxygen containing precursor, the aluminum containing precursor, and the second oxygen containing precursor until the desired thickness for film 140 containing HfAlO_3 is formed on the body region. A gate is formed over the gate dielectric 140. Typically, forming the gate includes forming a polysilicon layer, though a metal gate can be formed in an alternative process. Forming the substrate, source/drain regions, and the gate is performed using standard processes known to those skilled in the art. Additionally, the sequencing of the various elements of the process for forming a transistor is conducted with standard fabrication processes, also as known to those skilled in the art.

Embodiments of the method of forming a HfAlO_3 film by ALD as a gate dielectric can be applied to other transistor structures having dielectric layers. For example, Figure 4 depicts an embodiment of a configuration of a transistor 400 capable of being fabricated according to the teachings of the present invention. The transistor 400 includes a silicon based substrate 410 with two source/drain regions 420, 430 separated by a body region 432. The body region 432 between the two source/drain regions 420, 430 defines a channel region having a channel length 434. Located above the body region 432 is a stack 455

including a gate dielectric 440, a floating gate 452, a floating gate dielectric 442, and control gate 450. The gate dielectric 440 is formed in an ALD process according to the teachings of the present invention as described above with the remaining elements of the transistor 400 formed using processes known to those skilled in the art. Alternately, both the gate dielectric 440 and the floating gate dielectric 442 can be formed by ALD in accordance with the present invention as described above.

Transistors created by the methods described above may be implemented into memory devices and electronic systems including information handling devices. Information handling devices having a dielectric layer containing a HfAlO_3 film can be constructed using various embodiments of the methods described above. Such information devices include wireless systems, telecommunication systems, and computers. An embodiment of a computer having a dielectric layer containing a HfAlO_3 film is shown in Figures 5-7 and described below. While specific types of memory devices and computing devices are shown below, it will be recognized by one skilled in the art that several types of memory devices and electronic systems including information handling devices utilize the invention.

A personal computer, as shown in Figures 5 and 6, include a monitor 500, keyboard input 502 and a central processing unit 504. The processor unit 504 typically includes microprocessor 606, memory bus circuit 608 having a plurality of memory slots 612(a-n), and other peripheral circuitry 610. Peripheral circuitry 610 permits various peripheral devices 624 to interface processor-memory bus 620 over input/output (I/O) bus 622. The personal computer shown in Figures 5 and 6 also includes at least one transistor having a gate dielectric containing a HfAlO_3 film in an embodiment according to the teachings of the present invention.

Microprocessor 606 produces control and address signals to control the exchange of data between memory bus circuit 608 and microprocessor 606 and between memory bus circuit 608 and peripheral circuitry 610. This exchange of data is accomplished over high speed memory bus 620 and over high speed I/O bus 622.

Coupled to memory bus 620 are a plurality of memory slots 612(a-n) which receive memory devices well known to those skilled in the art. For example, single in-line memory modules (SIMMs) and dual in-line memory modules (DIMMs) may be used in the implementation of the present invention.

5 These memory devices can be produced in a variety of designs which provide different methods of reading from and writing to the dynamic memory cells of memory slots 612. One such method is the page mode operation. Page mode operations in a DRAM are defined by the method of accessing a row of a memory cell arrays and randomly accessing different columns of the array. Data
10 stored at the row and column intersection can be read and output while that column is accessed. Page mode DRAMs require access steps which limit the communication speed of memory circuit 608.

An alternate type of device is the extended data output (EDO) memory which allows data stored at a memory array address to be available as output
15 after the addressed column has been closed. This memory can increase some communication speeds by allowing shorter access signals without reducing the time in which memory output data is available on memory bus 620. Other alternative types of devices include SDRAM, DDR SDRAM, SLDRAM and Direct RDRAM as well as others such as SRAM or Flash memories.

20 Figure 7 illustrates a schematic view of an embodiment of a DRAM memory device 700 according to the teachings of the present invention. DRAM device 700 is compatible with memory slots 612(a-n). The description of DRAM 700 has been simplified for purposes of illustrating a DRAM memory device and is not intended to be a complete description of all the features of a
25 DRAM. Those skilled in the art will recognize that a wide variety of memory devices may be used in the implementation of the present invention. The example of a DRAM memory device shown in Figure 6 includes at least one transistor having a gate dielectric containing a HfAlO_3 film in an embodiment according to the teachings of the present invention.

30 Control, address and data information provided over memory bus 620 is further represented by individual inputs to DRAM 700, as shown in Figure 7.

These individual representations are illustrated by data lines 702, address lines 704 and various discrete lines directed to control logic 706.

As is well known in the art, DRAM 700 includes memory array 710 which in turn comprises rows and columns of addressable memory cells. Each memory cell in a row is coupled to a common word line. The word line is coupled to gates of individual transistors, where at least one transistor has a gate coupled to a gate dielectric containing HfAlO_3 in accordance with the method and structure previously described above. Additionally, each memory cell in a column is coupled to a common bit line. Each cell in memory array 710 includes a storage capacitor and an access transistor as is conventional in the art.

DRAM 700 interfaces with, for example, microprocessor 606 through address lines 704 and data lines 702. Alternatively, DRAM 700 may interface with a DRAM controller, a micro-controller, a chip set or other electronic system. Microprocessor 606 also provides a number of control signals to DRAM 700, including but not limited to, row and column address strobe signals RAS and CAS, write enable signal WE, an output enable signal OE and other conventional control signals.

Row address buffer 712 and row decoder 714 receive and decode row addresses from row address signals provided on address lines 704 by microprocessor 606. Each unique row address corresponds to a row of cells in memory array 710. Row decoder 714 includes a word line driver, an address decoder tree, and circuitry which translates a given row address received from row address buffers 712 and selectively activates the appropriate word line of memory array 710 via the word line drivers.

Column address buffer 716 and column decoder 718 receive and decode column address signals provided on address lines 704. Column decoder 718 also determines when a column is defective and the address of a replacement column. Column decoder 718 is coupled to sense amplifiers 720. Sense amplifiers 720 are coupled to complementary pairs of bit lines of memory array 710.

Sense amplifiers 720 are coupled to data-in buffers 722 and data-out buffers 724. Data-in buffers 722 and data-out buffers 724 are coupled to data lines 702. During a write operation, data lines 702 provide data to data-in

buffers 722. Sense amplifier 720 receives data from data-in buffers 722 and stores the data in memory array 710 as a charge on a capacitor of a cell at an address specified on address lines 704.

During a read operation, DRAM 700 transfers data to microprocessor 606 from memory array 710. Complementary bit lines for the accessed cell are equilibrated during a precharge operation to a reference voltage provided by an equilibration circuit and a reference voltage supply. The charge stored in the accessed cell is then shared with the associated bit lines. A sense amplifier of sense amplifiers 720 detects and amplifies a difference in voltage between the complementary bit lines. The sense amplifier passes the amplified voltage to data-out buffers 724.

Control logic 706 is used to control the many available functions of DRAM 700. In addition, various control circuits and signals not detailed herein initiate and synchronize DRAM 700 operation as known to those skilled in the art. As stated above, the description of DRAM 700 has been simplified for purposes of illustrating the present invention and is not intended to be a complete description of all the features of a DRAM. Those skilled in the art will recognize that a wide variety of memory devices, including but not limited to, SDRAMs, SLDRAMs, RDRAMs and other DRAMs and SRAMs, VRAMs and EEPROMs, may be used in the implementation of the present invention. The DRAM implementation described herein is illustrative only and not intended to be exclusive or limiting.

Conclusion

A gate dielectric containing HfAlO_3 and a method of fabricating such a gate produces a reliable gate dielectric having an equivalent oxide thickness thinner than attainable using SiO_2 . HfAlO_3 gate dielectrics formed using the methods described herein are thermodynamically stable such that the gate dielectrics formed will have minimal reactions with a silicon substrate or other structures during processing.

Transistors, higher level ICs or devices, and systems are constructed utilizing the novel process for forming a gate dielectric having an ultra thin equivalent oxide thickness, t_{eq} . Gate dielectric layers or films containing HfAlO_3

are formed having a high dielectric constant (κ), where the gate dielectrics are capable of a t_{eq} thinner than 10 Å, thinner than the expected limit for SiO₂ gate dielectrics. At the same time, the physical thickness of the HfAlO₃ layer is much larger than the SiO₂ thickness associated with the t_{eq} limit of SiO₂. Forming the
5 larger thickness provides advantages in processing the gate dielectric. In addition forming a dielectric containing HfAlO₃, Al₂O₃, and HfO₂ through controlling a hafnium sequence and a aluminum sequence in an ALD processing of a substrate allows the selection of a dielectric constant ranging from that of Al₂O₃ to the dielectric constant of HfO₂.

10 Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that any arrangement which is calculated to achieve the same purpose may be substituted for the specific embodiment shown. This application is intended to cover any adaptations or variations of the present invention. It is to be understood that the
15 above description is intended to be illustrative, and not restrictive.

Combinations of the above embodiments, and other embodiments will be apparent to those of skill in the art upon reviewing the above description. The scope of the invention includes any other applications in which the above structures and fabrication methods are used. The scope of the invention should
20 be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.

What is claimed is:

1. A method of forming an electronic device comprising:
pulsing a hafnium containing precursor into a reaction chamber containing a
5 substrate; and
pulsing an aluminum containing precursor into the reaction chamber to form
a dielectric film.
2. The method of claim 1, wherein pulsing a hafnium containing precursor into
10 a reaction chamber containing a substrate, and pulsing an aluminum containing
precursor into the reaction chamber are elements of an atomic layer deposition
process.
3. The method of claim 1 or 2, wherein forming the electronic device includes
15 forming a transistor, the method further including:
forming first and second source/drain regions in a substrate;
forming a body region between the first and second source/drain regions;
pulsing the hafnium containing precursor into the reaction chamber and
pulsing
20 the aluminum containing precursor to form the dielectric film on the body region
between the first and second source/drain regions; and
coupling a gate to the dielectric film.
4. The method of claim 1 or 2, wherein forming the electronic device includes
25 forming a memory device having at least one access transistor having a film
containing HfAlO_3 on a body region between a first and second source/drain
regions, wherein forming the film includes the pulsing of the hafnium containing
precursor and the pulsing of the aluminum containing precursor.

5. The method of claim 4, wherein the method further includes
forming a number of access transistors;
forming a number of word lines coupled to a number of the gates of the
number of access transistors;
5 forming a number of source lines coupled to a number of the first
source/drain regions of the number of access transistors; and
forming a number of bit lines coupled to a number of the second
source/drain regions of the number of access transistors.
- 10 6. The method of claim 1 or 2, wherein forming the electronic device includes
forming an electronic system including:
providing a processor;
coupling a memory device to the processor, wherein one of the memory
device or the processor has at least one transistor having a film containing HfAlO_3
15 on a body region between a first and second source/drain regions, the film
containing HfAlO_3 formed by the pulsing of the hafnium containing precursor into a
reaction chamber and the pulsing of the aluminum containing precursor into the
reaction the chamber; and
forming a system bus that couples the processor to the memory array.
20
7. The method of claim 1, 2, 3, 4, or 6, wherein pulsing a hafnium containing
precursor into a reaction chamber is followed by pulsing a first oxygen containing
precursor into the reaction chamber and pulsing an aluminum containing
precursor into the reaction chamber is followed by pulsing a second oxygen
25 containing precursor into the reaction chamber.
8. The method of claim 7, wherein pulsing a first oxygen containing precursor
includes pulsing water vapor.

9. The method of claim 7, wherein pulsing a second oxygen containing precursor includes pulsing distilled water vapor.

10. The method of claim 7, wherein pulsing a second oxygen containing precursor includes pulsing oxygen.

11. The method of claim 1, 2, 3, 4, or 6, wherein pulsing each precursor into the reaction chamber is controlled for a predetermined period, the predetermined period being individually controlled for each precursor pulsed into the reaction chamber.

10

12. The method of claim 1, 2, 3, 4, or 6, wherein the method further includes maintaining the substrate at a selected temperature for each pulsing of a precursor, the selected temperature set independently for pulsing each precursor.

13. The method of claim 1, 2, 3, 4, or 6, wherein each pulsing of a precursor is followed by purging the reaction chamber with a purging gas.

14. The method of claim 1, 2, 3, 4, or 6, wherein the method further includes repeating for a number of cycles the pulsing of the hafnium containing precursor, and the aluminum containing precursor.

20

15. The method of claim 14, wherein repeating for a number of cycles the pulsing of the hafnium containing precursor and the aluminum containing precursor is followed by annealing at a temperature ranging from about 300°C to about 800°C.

25

16. The method of claim 1, 2, 3, 4, or 6, wherein the method further includes for each precursor independently controlling a pulsing period of time, a number of times the precursor is pulsed into the substrate, and a substrate temperature to form

a dielectric film containing HfAlO_3 , the dielectric film having a dielectric constant in the range from about 9 to about 25.

17. The method of claim 16, wherein the forming the dielectric film containing
5 HfAlO_3 includes forming an essentially HfAlO_3 film.

18. The method of claim 1, 2, 3, 4, or 6, wherein pulsing a hafnium containing precursor includes pulsing a HfCl_4 precursor.

10 19. The method of claim 18, wherein pulsing a HfCl_4 precursor into a reaction chamber is performed with the substrate maintained at a temperature ranging from about 350°C to about 550°C .

20. The method of claim 18, wherein pulsing a HfCl_4 precursor into a reaction
15 chamber is performed with the HfCl_4 precursor temperature ranging from about 130°C to about 154°C .

21. The method of claim 18, wherein the method further includes after pulsing a HfCl_4 precursor pulsing a first oxygen containing precursor into the reaction
20 chamber at a flow rate ranging from about $0.5 \text{ mPa m}^3/\text{sec}$ to about $1.0 \text{ mPa m}^3/\text{sec}$.

22. The method of claim 1, 2, 3, 4, or 6, wherein pulsing an aluminum containing precursor includes pulsing a trimethylaluminium precursor into the reaction chamber.

25

23. The method of claim 22, wherein pulsing the trimethylaluminium precursor into the reaction chamber is performed with the substrate maintained at a temperature ranging from about 350°C to about 370°C .

24. The method of claim 22, wherein pulsing a trimethylaluminium precursor into the reaction chamber is performed at a pressure of about 230 mTorr.

25. The method of claim 1, 2, 3, 4, or 6, wherein pulsing an aluminum
5 containing precursor includes pulsing a DMEAA precursor into the reaction chamber.

26. The method of claim 25, wherein pulsing a DMEAA precursor into the reaction chamber is performed with the substrate maintained at a temperature
10 ranging from about 350°C to about 550°C.

27. The method of claim 25, wherein pulsing a DMEAA precursor into the reaction chamber is performed at a pressure of about 30 mTorr.

15 28. The method of claim 1, 2, 3, 4, or 6, wherein pulsing a hafnium containing precursor includes pulsing a HfCl_4 precursor and pulsing an aluminum containing precursor includes pulsing a trimethylaluminium precursor into the reaction chamber.

20 29. The method of claim 28, wherein pulsing a trimethylaluminium precursor into the reaction chamber is followed by purging the reaction chamber with argon.

30. The method of claim 1, 2, 3, 4, or 6, wherein pulsing a hafnium containing precursor includes pulsing a HfCl_4 precursor and pulsing an aluminum containing
25 precursor includes pulsing a DMEAA precursor into the reaction chamber.

31. The method of claim 28 or 30, wherein pulsing a HfCl_4 precursor into a reaction chamber is followed by purging the reaction chamber with pure nitrogen.

32. The method of claim 30, wherein pulsing a DMEAA precursor into the reaction chamber is followed by purging the reaction chamber with hydrogen.

33. An electronic device formed by the method of claim 1, 2, 3, 4, 6, 18, 22, 25,
5 28, or 30.

34. An electronic device comprising:
at least one transistor having a body region between a first and a second
source/drain regions, a dielectric film on the body region, and a gate coupled to the
10 dielectric film;
characterized in that
the dielectric film contains atomic layer deposited HfAlO_3 .

35. The electronic device of claim 34, wherein the electronic device is a memory
15 device.

36. The electronic device of claim 35, wherein the memory further includes:
a number of access transistors;
a number of word lines coupled to a number of the gates of the number of
20 access transistors;
a number of source lines coupled to a number of the first source/drain
regions of the number of access transistors; and
a number of bit lines coupled to a number of the second source/drain regions
of the number of access transistors.

25 37. The electronic device of claim 34, wherein the electronic device is an
electronic system having a processor coupled to a memory device.

38. The electronic device of claim 34, 35, or 37, wherein the dielectric film includes Al_2O_3 and HfO_2 .
39. The electronic device of claim 34, 35, or 37, wherein the dielectric film is
5 substantially amorphous.
40. The electronic device of claim 34, 35, or 37, wherein the dielectric film exhibits a dielectric constant in the range from about 9 to about 25.
- 10 41. The electronic device of claim 34, 35, or 37, wherein the dielectric film exhibits an equivalent oxide thickness (t_{eq}) in the range from about 3 Angstroms to about 12 Angstroms.
42. The electronic device of claim 34, 35, or 37, wherein the dielectric film
15 exhibits an equivalent oxide thickness (t_{eq}) of less than 3 Angstroms.

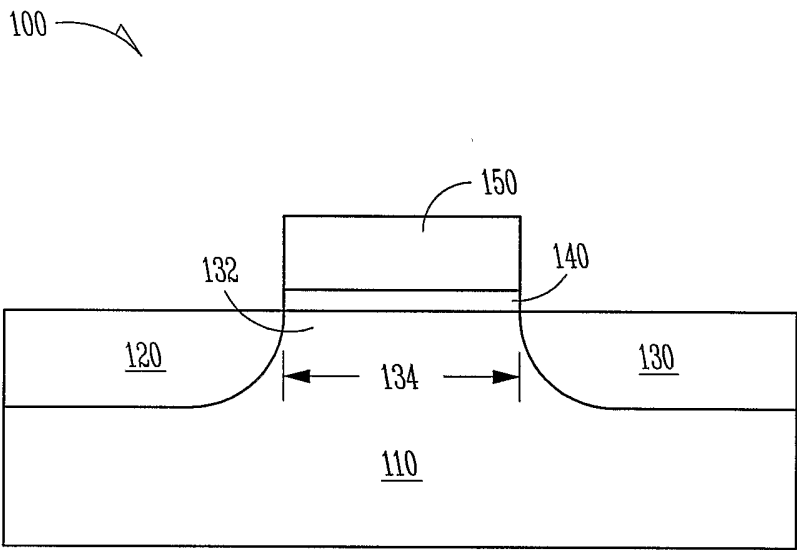


Fig.1

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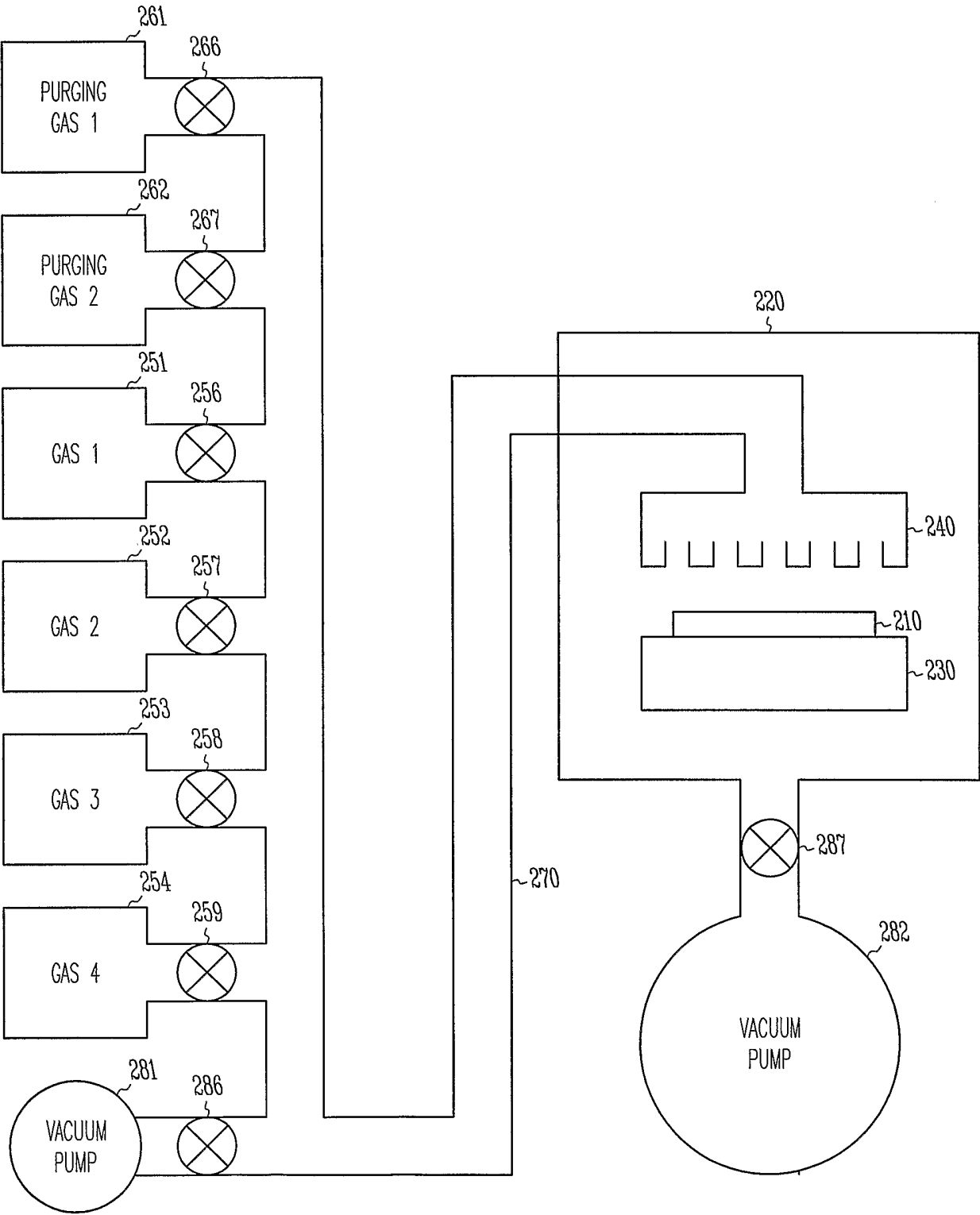


Fig.2A

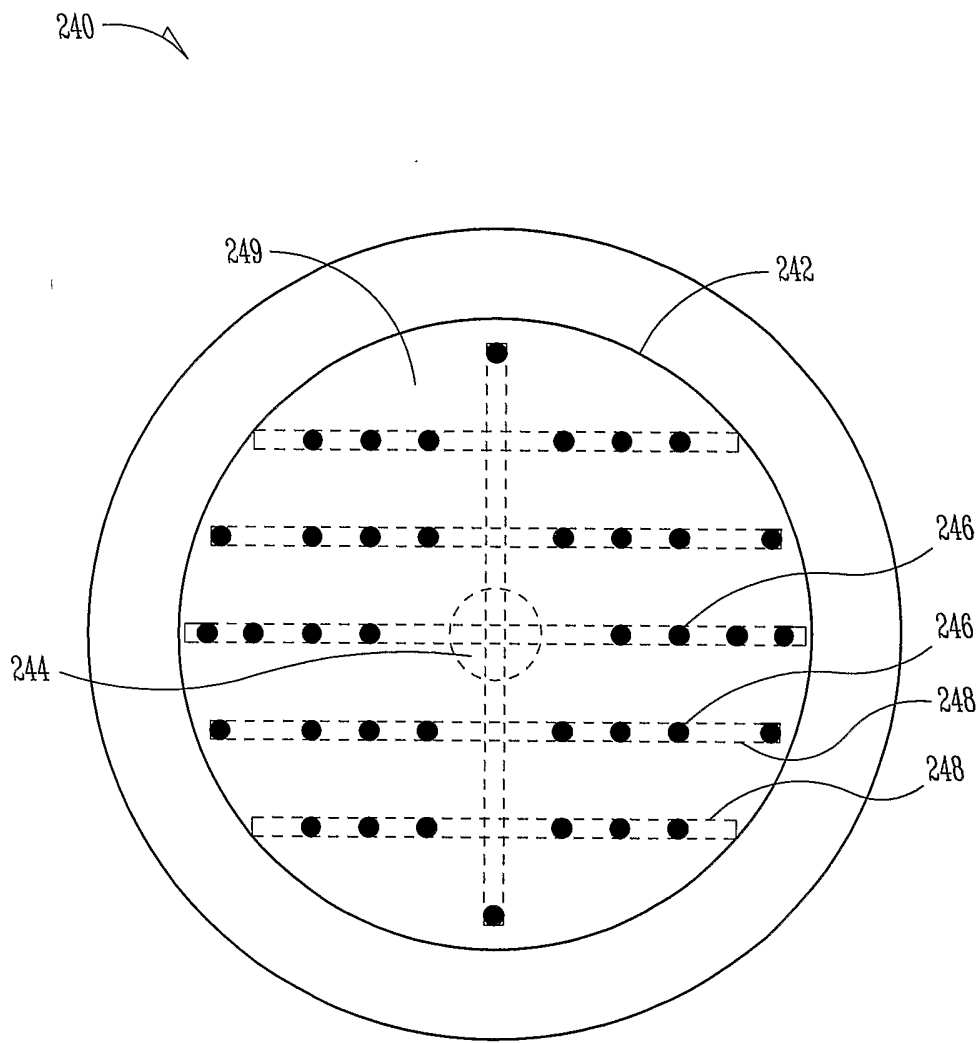


Fig.2B

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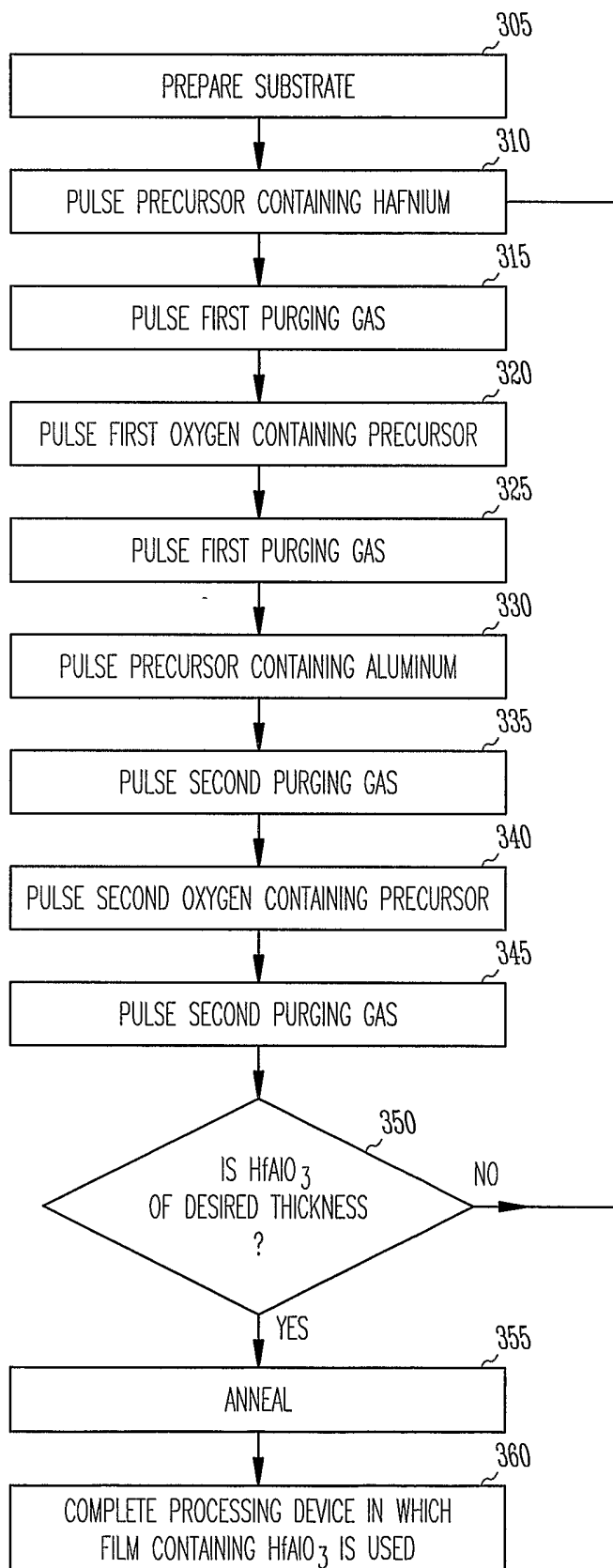


Fig.3

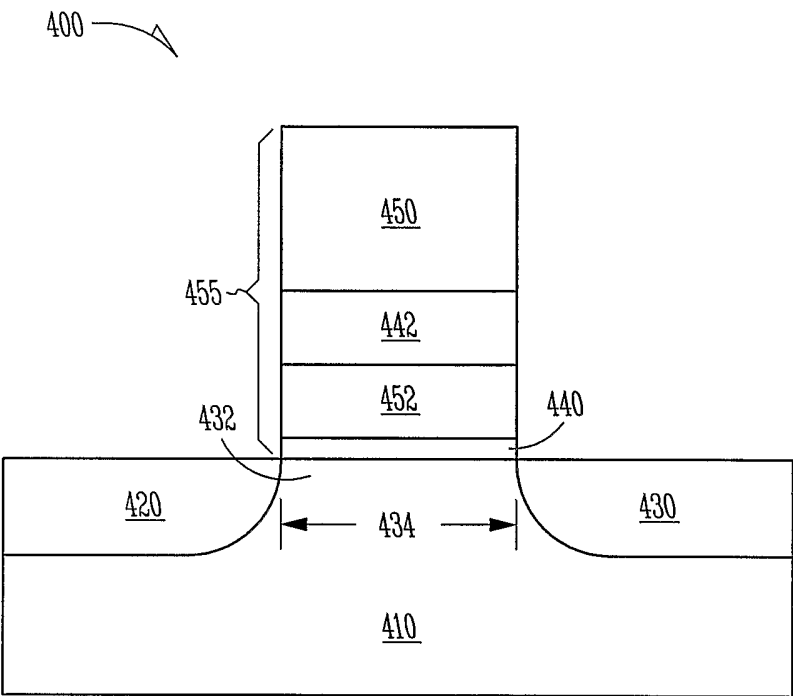


Fig.4

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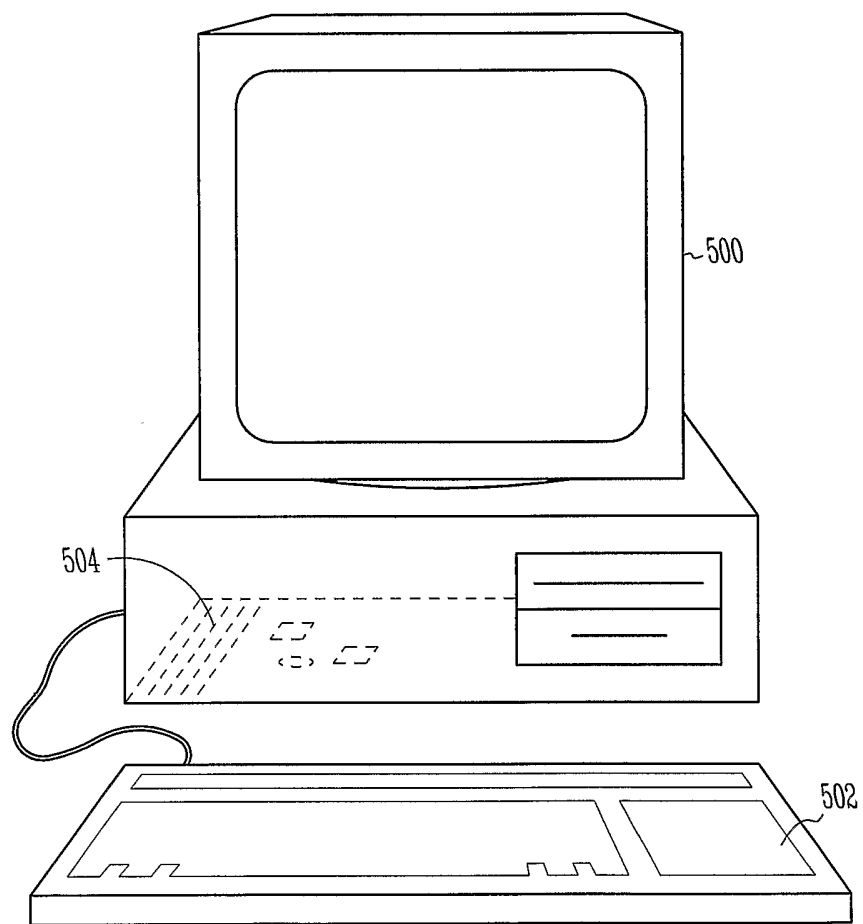


Fig.5

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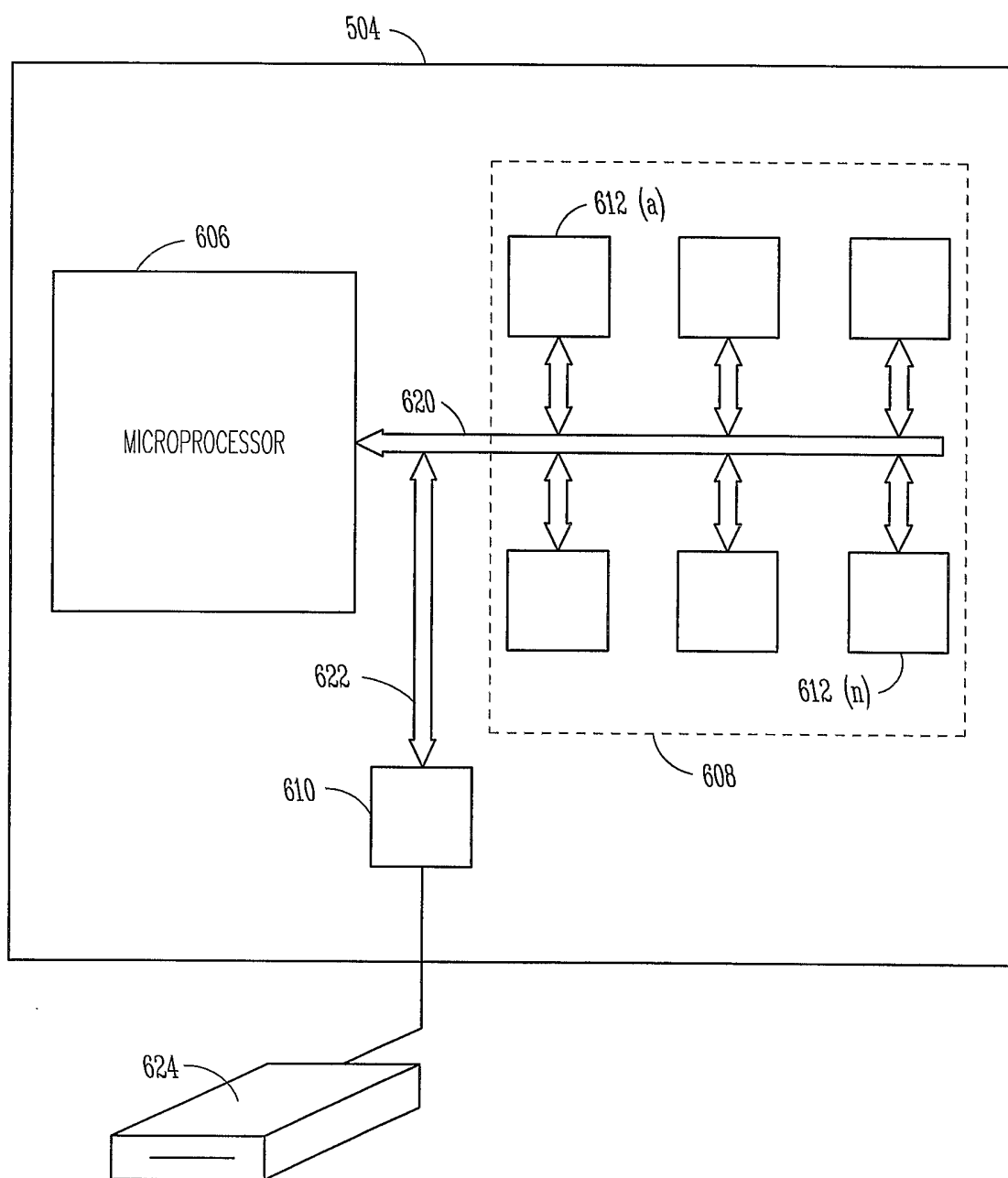


Fig.6

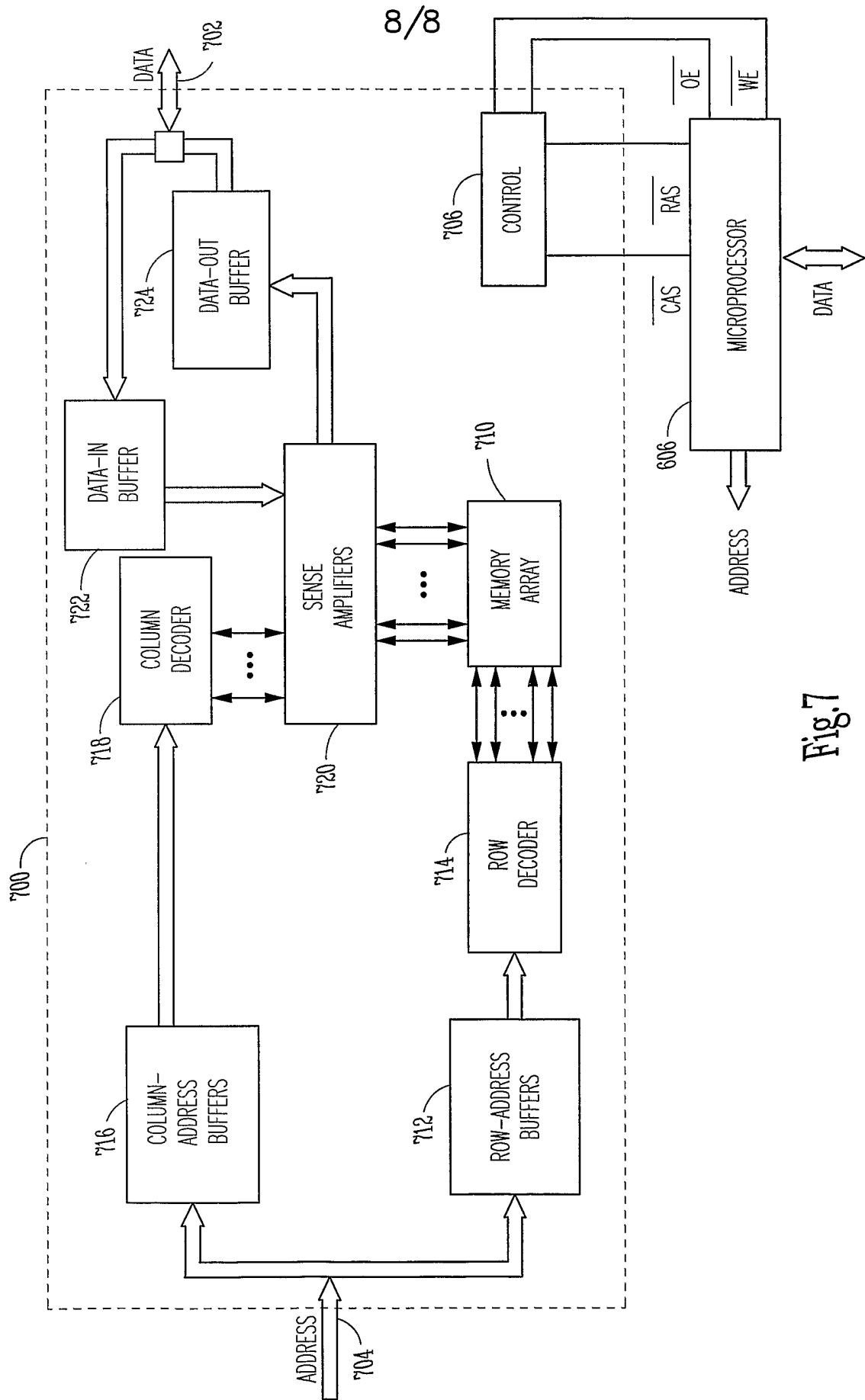


Fig.7

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US 03/17730

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L21/28 H01L29/51

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 297 539 B1 (MA YANJUN ET AL) 2 October 2001 (2001-10-02)	1-6, 11-24, 28, 29, 31, 33-42
Y	the whole document ----- -/--	7-10, 25-27, 30

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Nesso, S

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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