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**Chin et al.**

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- (54) **FLASH MEMORY**
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- (\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 192 days.

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(21) Appl. No.: **13/308,959**

Tsai et al., "Highly-Scaled 3.6-nm ENT Trapping Layer MONOS Device with Good Retention and Endurance", IEDM Tech. Dig., pp. 110-113 (2010).

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(65) **Prior Publication Data**

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*Primary Examiner* — Jerome Jackson, Jr.

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**H01L 29/792** (2006.01)

*Assistant Examiner* — Bo Fan

(52) **U.S. Cl.**  
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257/E21.409; 257/E21.546; 257/E27.062;  
438/586; 438/201; 438/268; 438/559; 438/381

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(58) **Field of Classification Search**  
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H01L 27/11563; H01L 29/4234; H01L  
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USPC ..... 257/324, 213, 287, 311, 411, 515, 325,  
257/E21.21, E29.309, E21.409, E21.546,  
257/E27.062, E29.264; 438/466, 585, 272,  
438/287, 552, 559, 381, 515  
See application file for complete search history.

(57) **ABSTRACT**

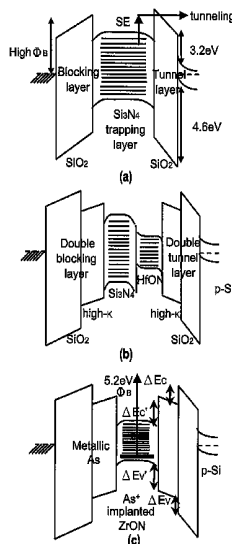
A MONOS Charge-Trapping flash (CTF), with record thinnest 3.6 nm ENT trapping layer, has a large 3.1 V 10-year extrapolated retention window at 125° C. and excellent 10<sup>6</sup> endurance at a fast 100 μs and ±16 V program/erase. This is achieved using As<sup>+</sup>-implanted higher κ trapping layer with deep 5.1 eV work-function of As. In contrast, the un-implanted device only has a small 10-year retention window of 1.9 V at 125° C. A MoN—[SiO<sub>2</sub>—LaAlO<sub>3</sub>]—[Ge—HfON]—[LaAlO<sub>3</sub>—SiO<sub>2</sub>]—Si CTF device is also provided with record-thinnest 2.5-nm Equivalent-Si<sub>3</sub>N<sub>4</sub>-Thickness (ENT) trapping layer, large 4.4 V initial memory window, 3.2 V 10-year extrapolated retention window at 125° C., and 3.6 V endurance window at 10<sup>6</sup> cycles, under very fast 100 μs and low ±16 V program/erase. These were achieved using Ge reaction with HfON trapping layer for better charge-trapping and retention.

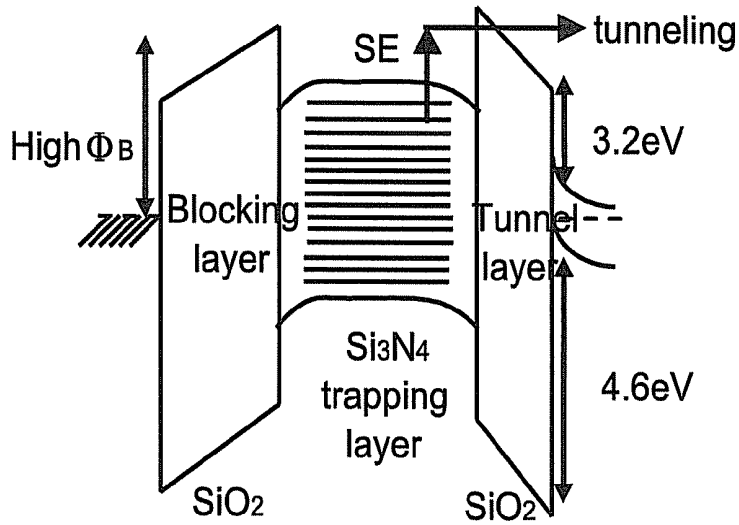
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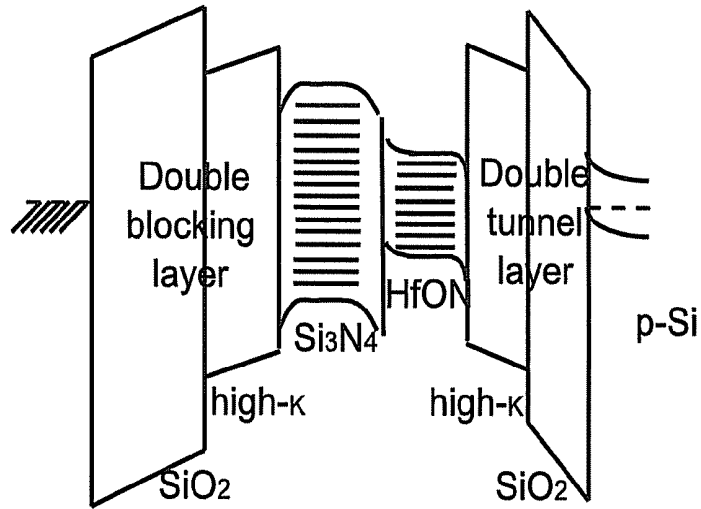
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**11 Claims, 10 Drawing Sheets**

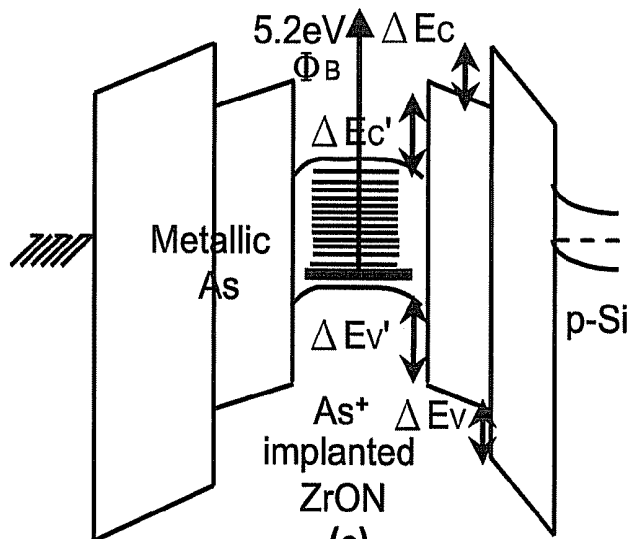




(a)



(b)



(c)

FIG.1

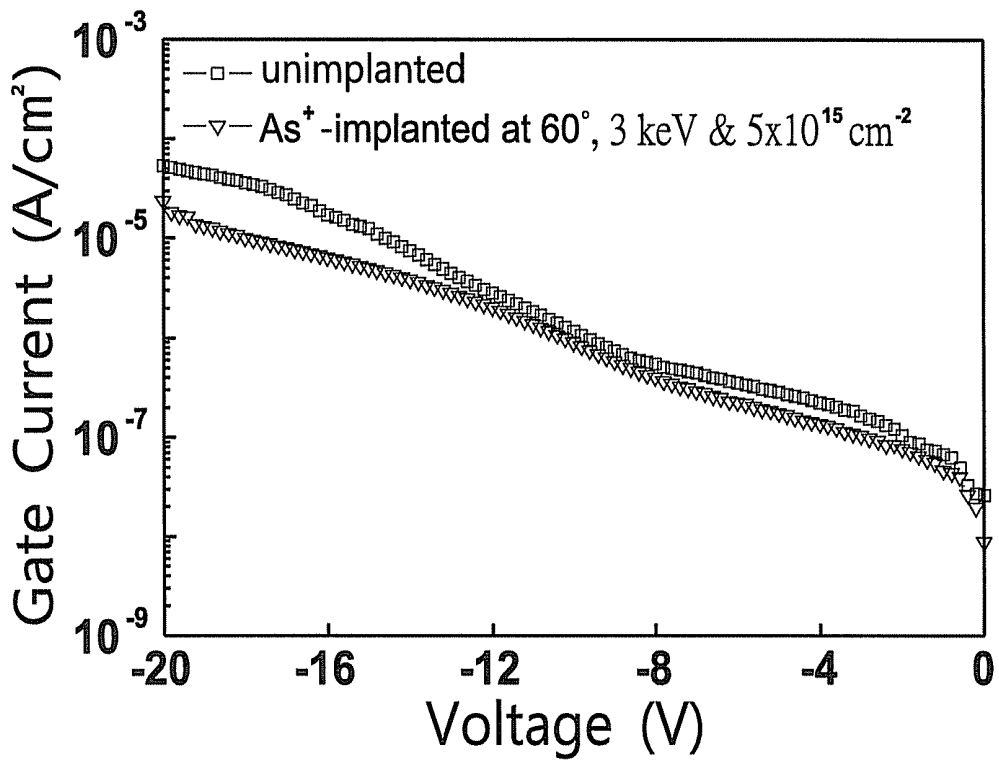


FIG. 2

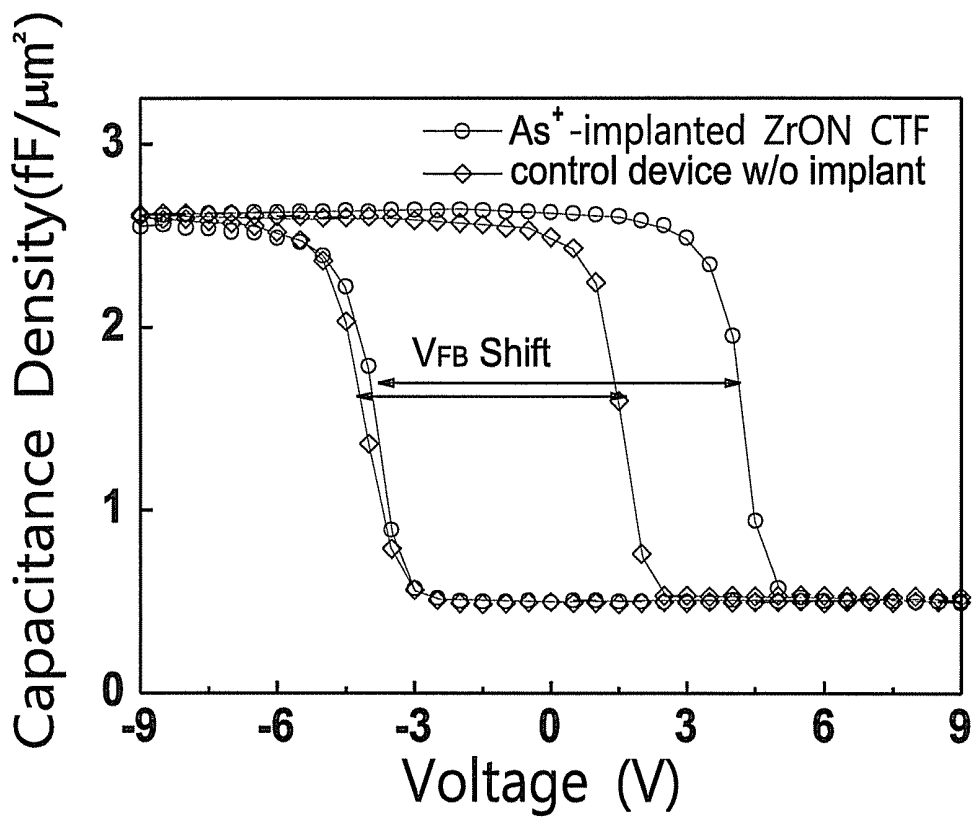


FIG. 3

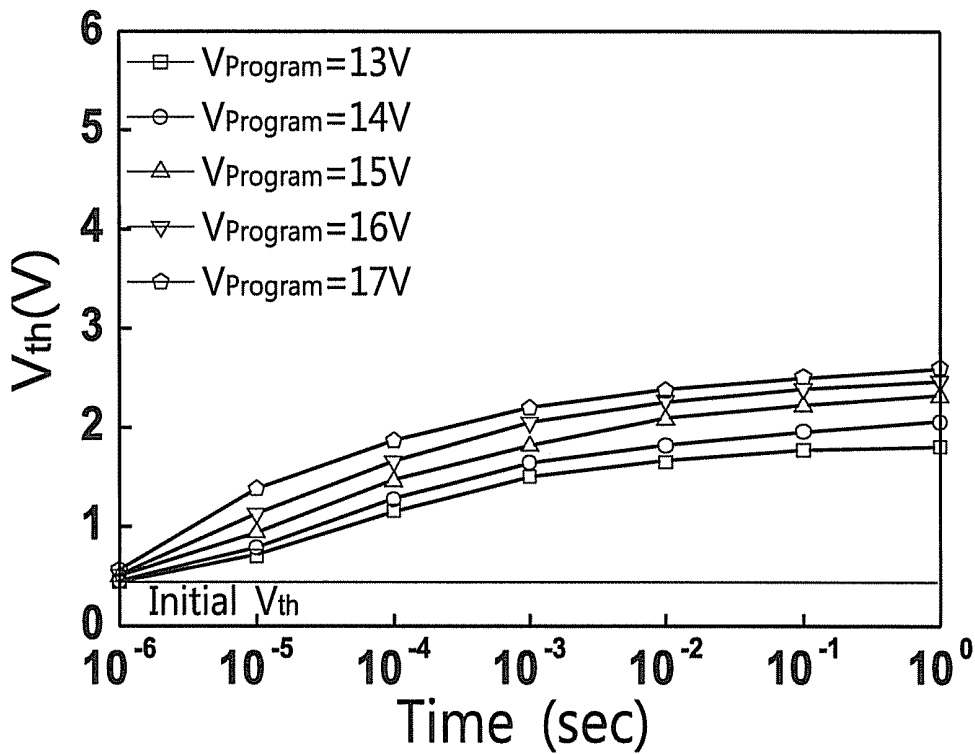


FIG. 4

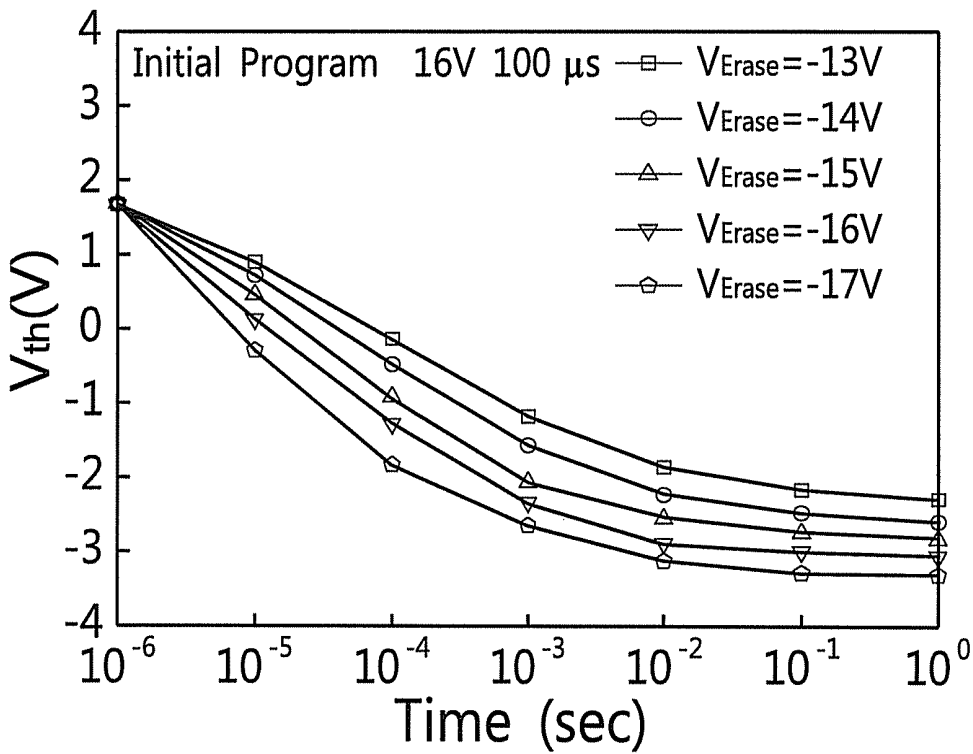


FIG. 5

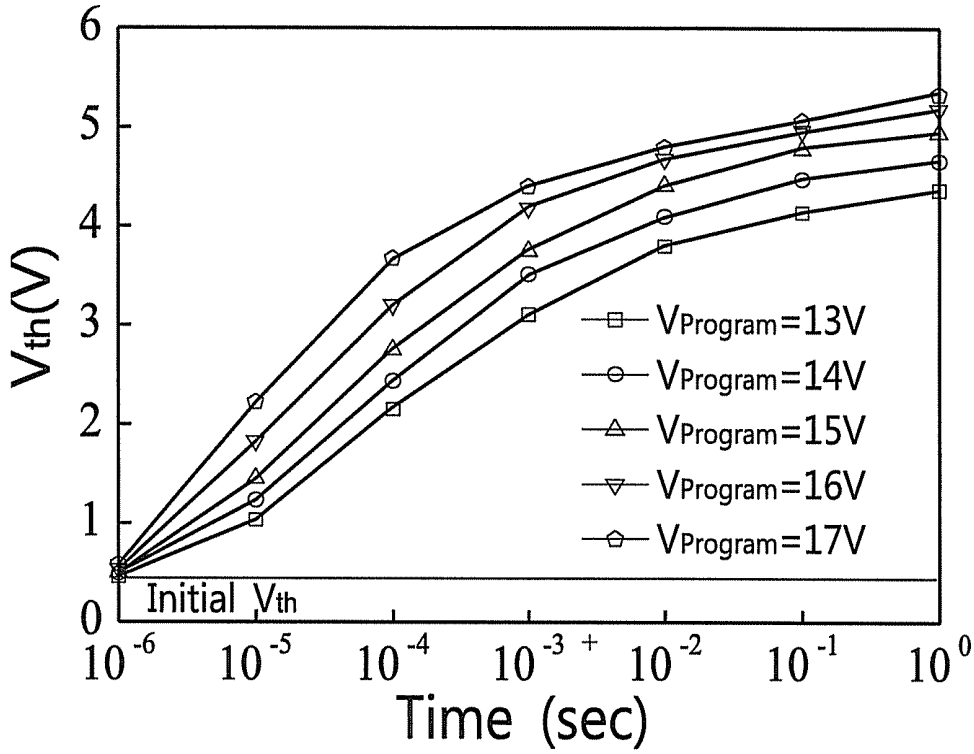


FIG. 6

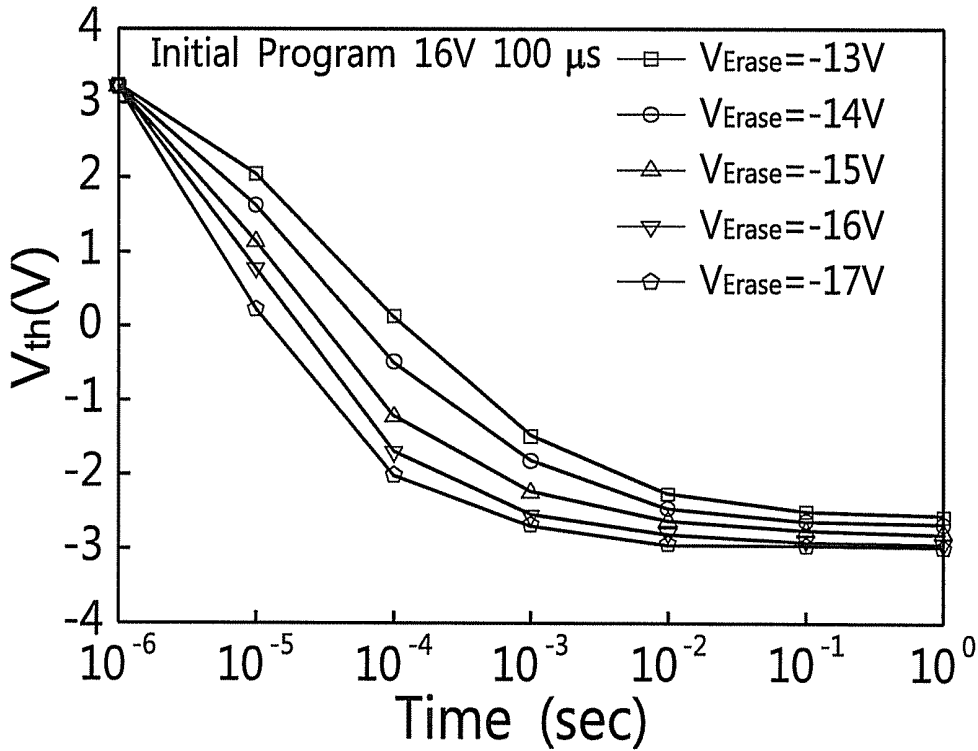


FIG. 7

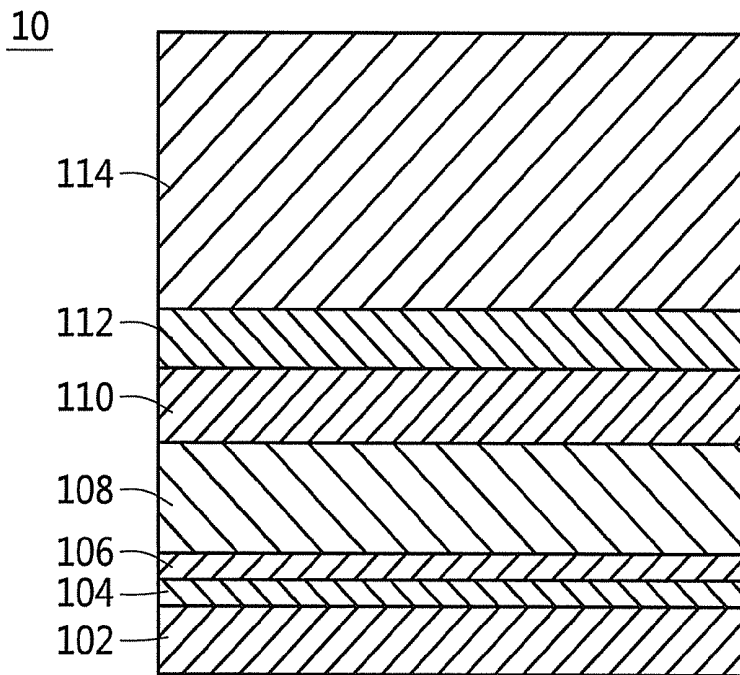


FIG. 8

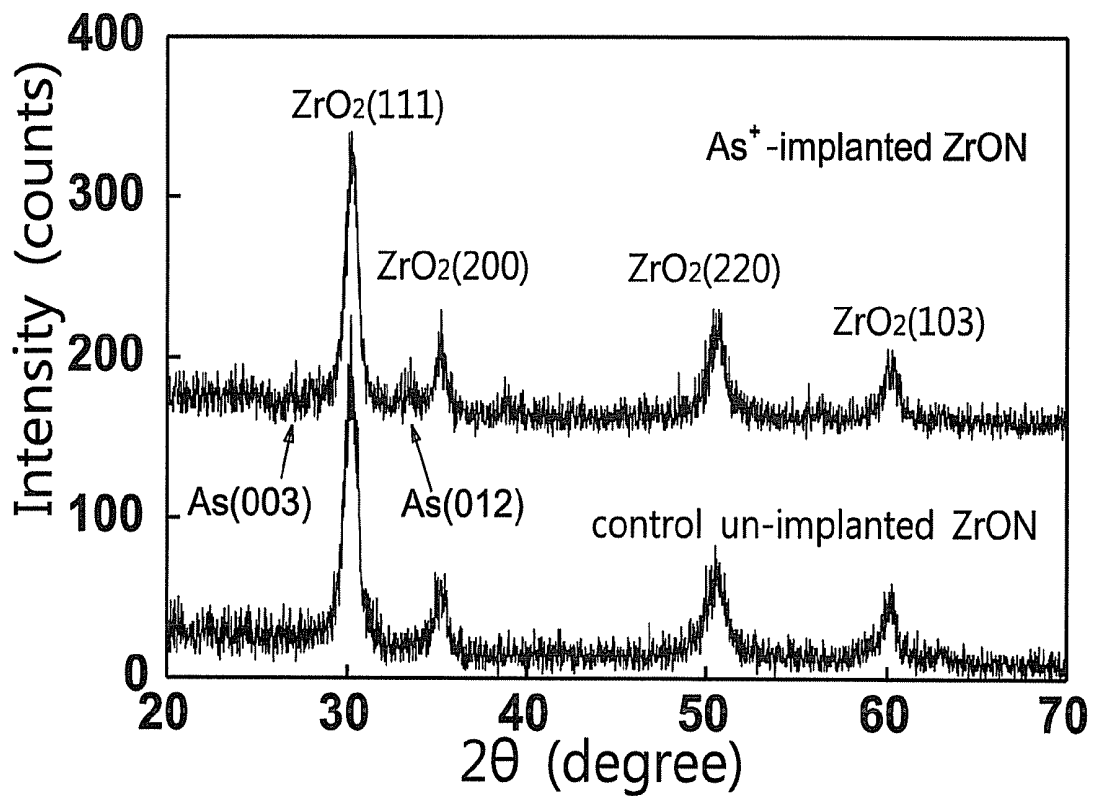


FIG. 9

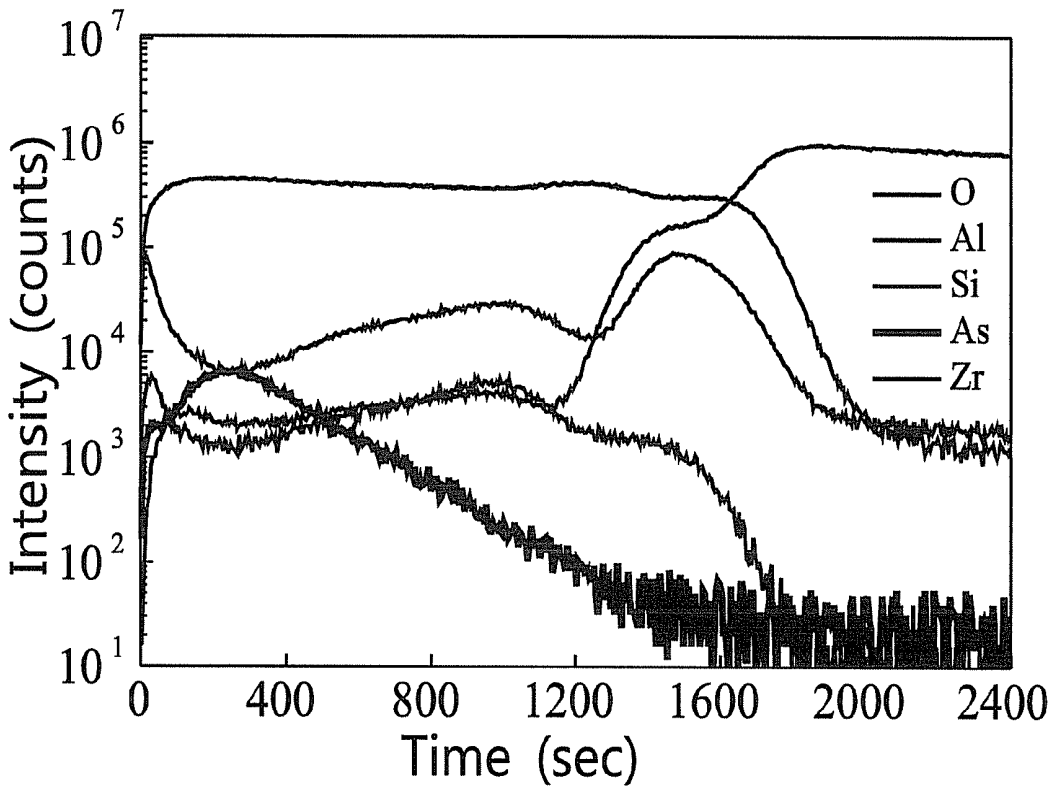


FIG. 10

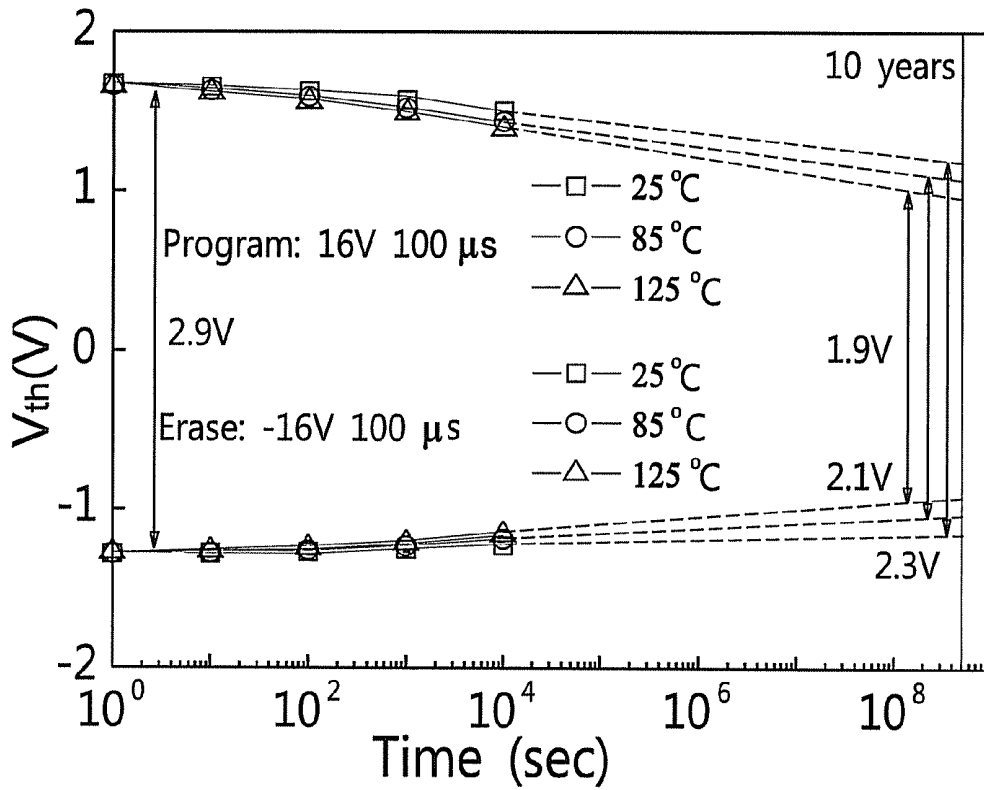


FIG. 11

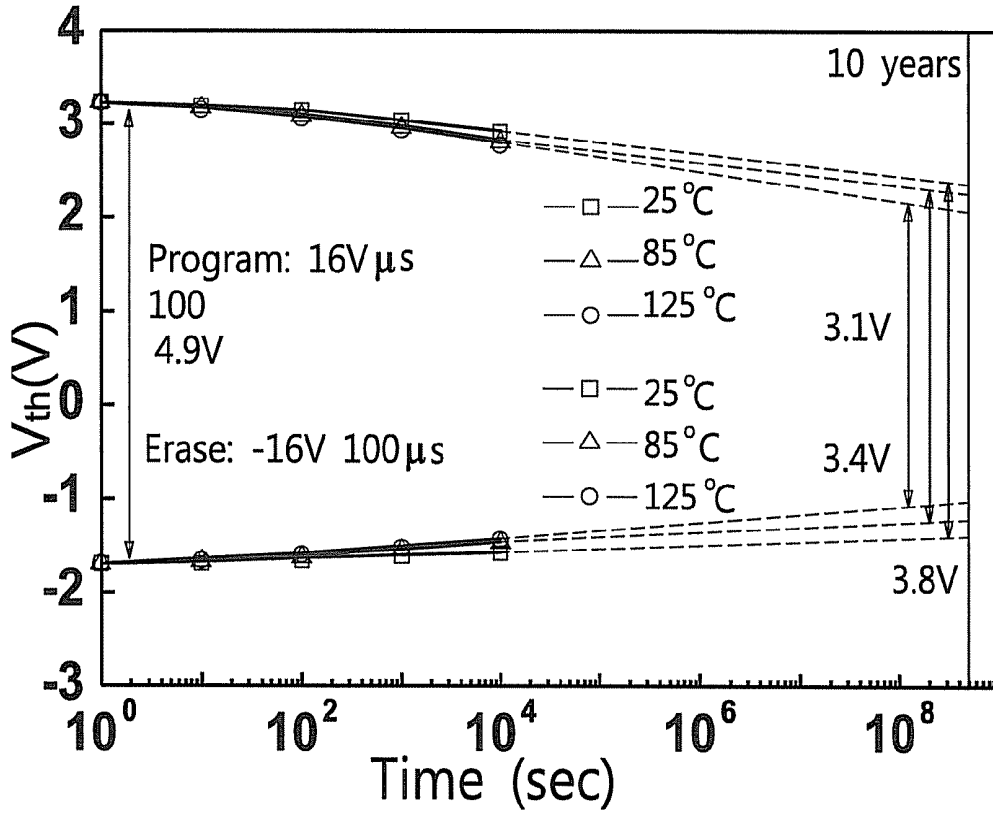


FIG. 12

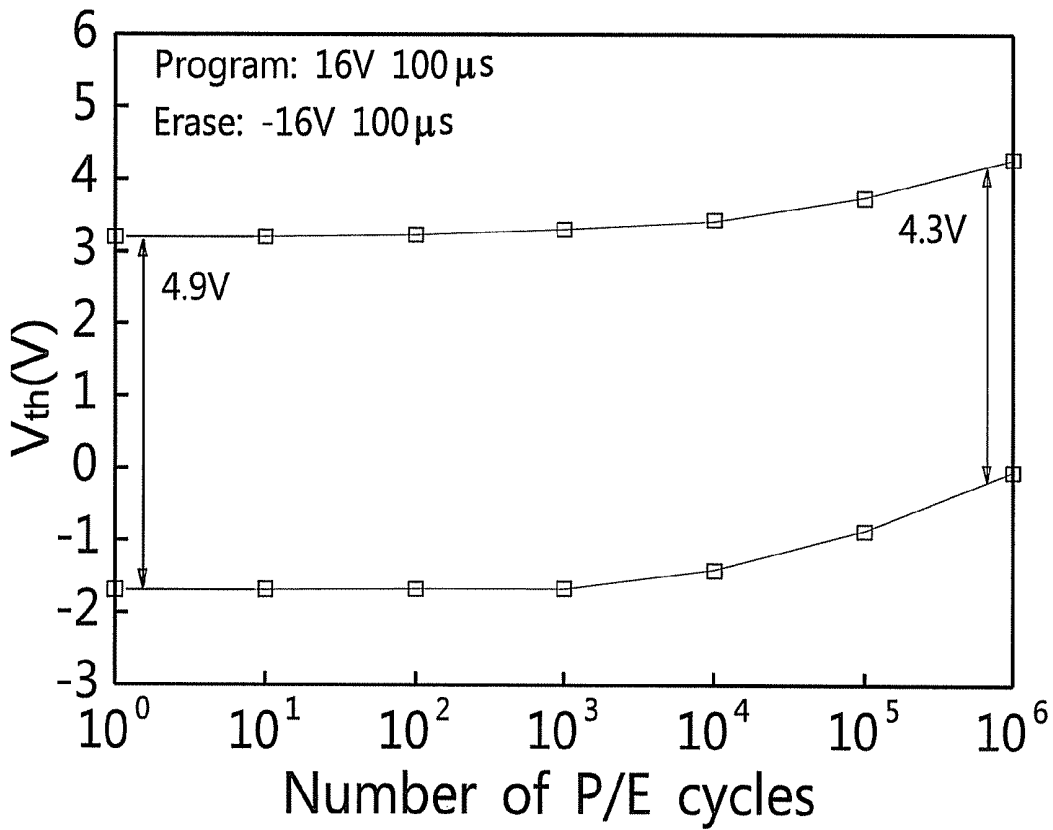
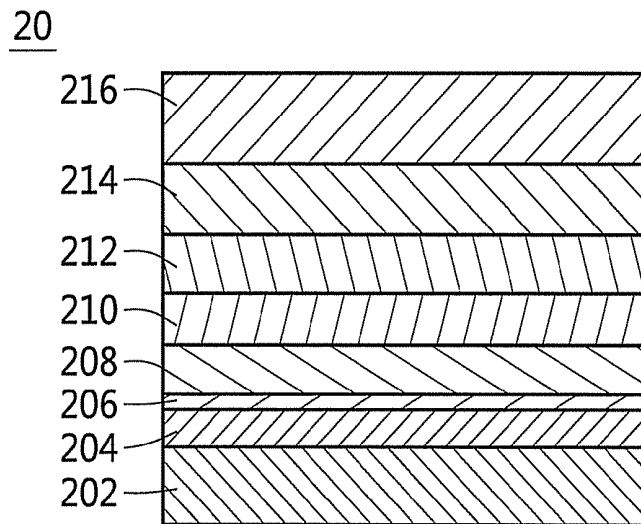
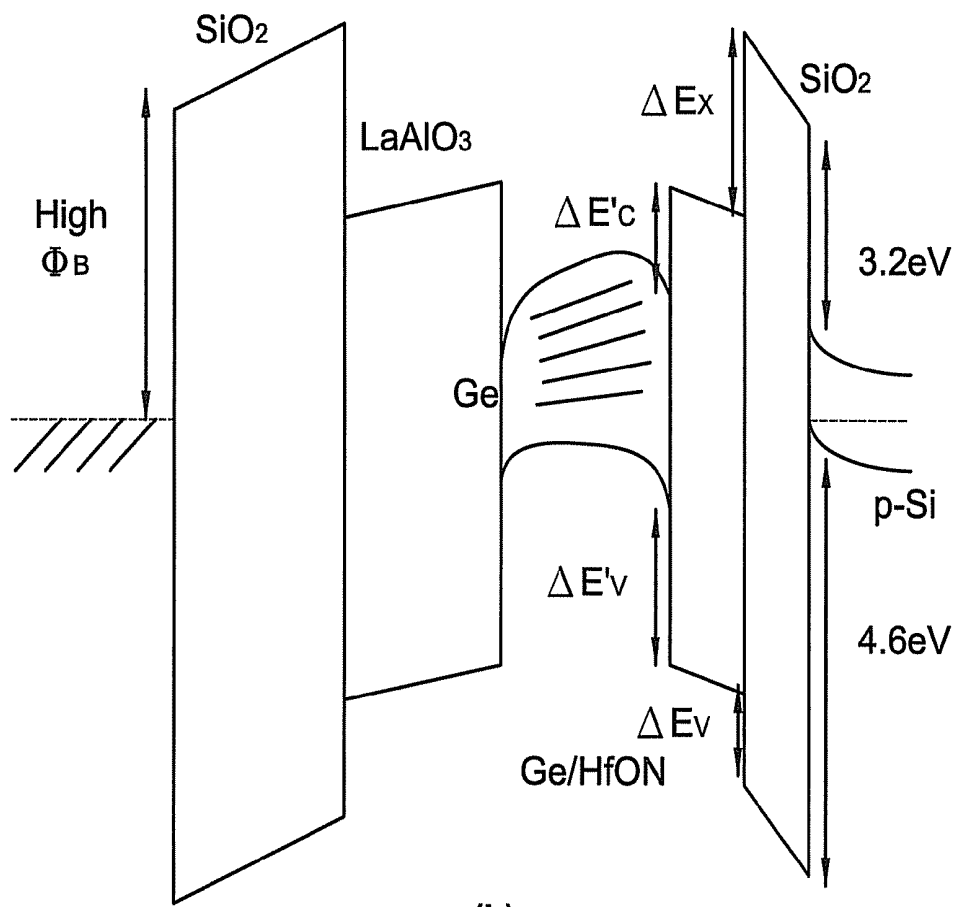


FIG. 13





(a)



(b)

FIG. 14

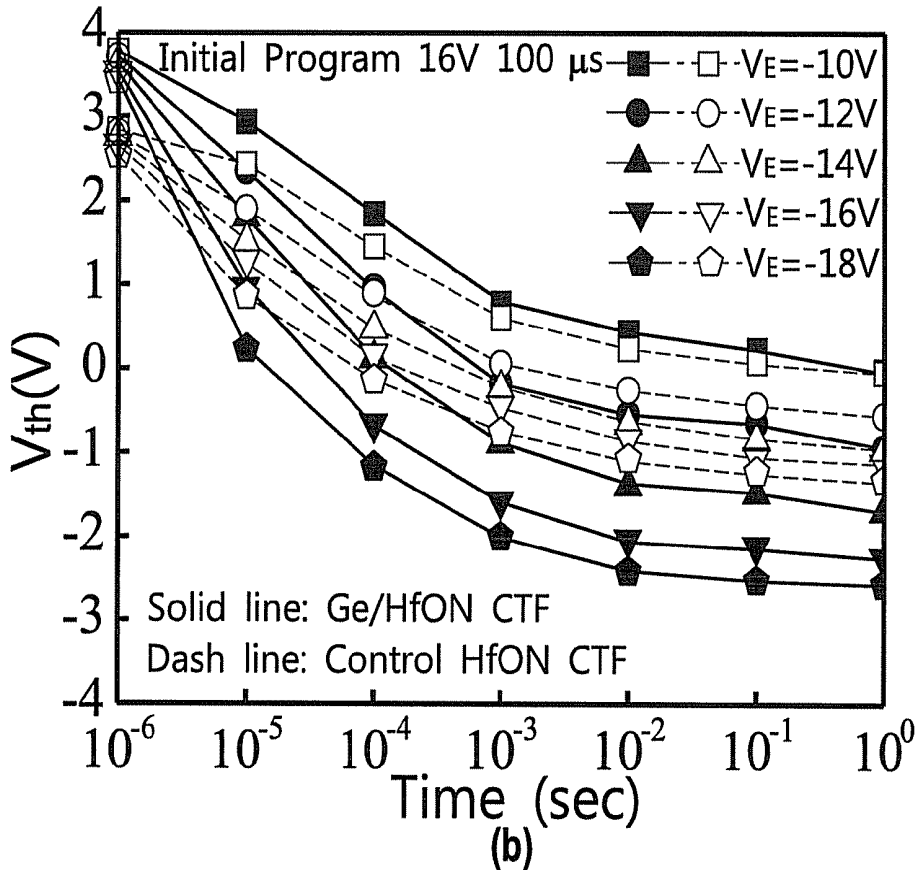
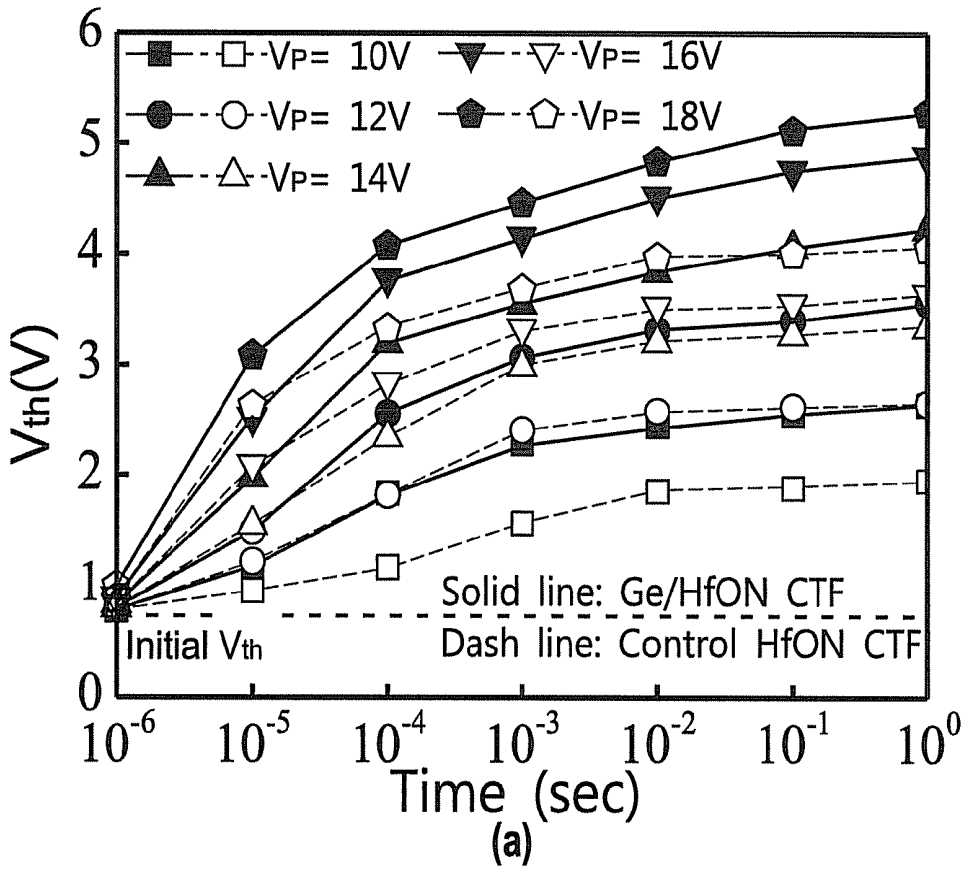


FIG. 15

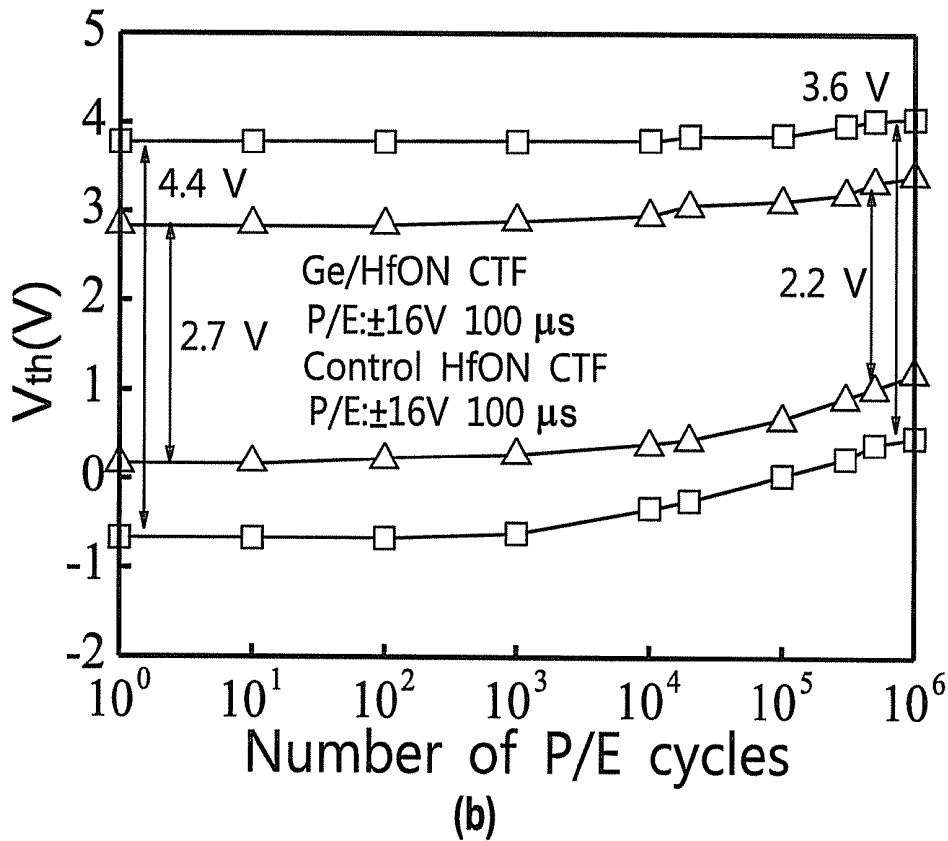
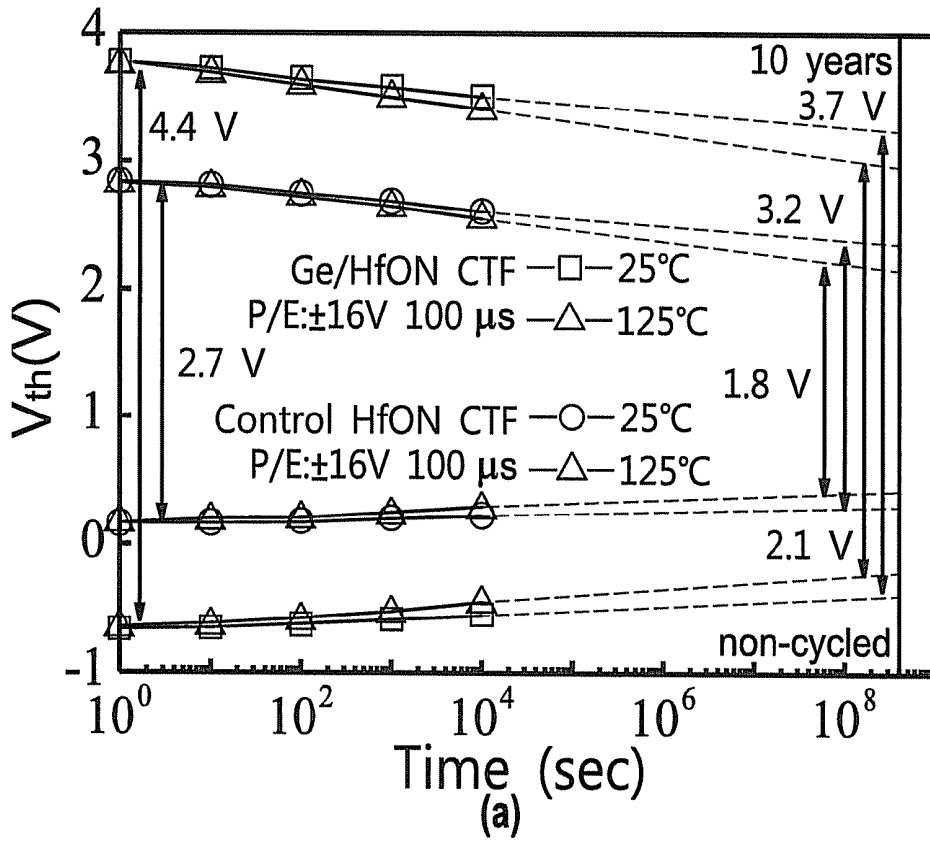


FIG. 16

## FLASH MEMORY

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

This invention relates to flash memories, and, more particularly, to a flash memory having a charge-trapping layer formed by implanting arsenic into ZrON.

## 2. Description of Related Art

According to International Technology Roadmap for Semiconductors (ITRS), the degraded endurance and retention are the toughest challenges to further down-scaling the Charge-Trapping Flash (CTF), due to the fewer electrons stored in highly scaled device. On the other hand, scaling down the Si<sub>3</sub>N<sub>4</sub> charge-trapping layer to 3-4 nm is needed in ITRS for continuous device scaling, but no proposed solution up to now. However, this worsens the retention and endurance due to the poorer trapping capability at thinner Si<sub>3</sub>N<sub>4</sub>, where nearly no charge trapping was found in 2 nm Si<sub>3</sub>N<sub>4</sub>. Although the retention is improved by using a thicker tunnel oxide, this yields reduced erase speed. Such retention and erase-speed trade-off is a basic limitation of CTF.

Previously we addressed this limitation with a deep trapping energy  $E_{vac}-E_C$  Al(Ga)N or HfON in a metal-oxide-nitride-oxide-Si (MONOS) device. The better retention of high- $\kappa$  Al(Ga)N MONOS CTF was also listed in ITRS. One drawback of desired higher  $\kappa$  HfON is the lower trapping efficiency; thus, the double trapping HfON—Si<sub>3</sub>N<sub>4</sub> CTF was used. Yet the scaling equivalent-Si<sub>3</sub>N<sub>4</sub>-thickness (ENT) is still limited to 7 nm.

## SUMMARY OF THE INVENTION

In view of the above-mentioned problems of the prior art, it is a primary objective of the present invention to provide flash memory that has a charge-trapping layer formed by implanting arsenic into ZrON.

In an embodiment of the present invention, the flash memory includes: a substrate; a first SiO<sub>2</sub> layer formed on the substrate; a first high- $\kappa$  layer formed on the first SiO<sub>2</sub> layer; a metal-implanted oxynitride layer formed on the first high- $\kappa$  layer; a second high- $\kappa$  layer formed on the metal-implanted oxynitride layer; a second SiO<sub>2</sub> layer formed on the second high- $\kappa$  layer; and a gate layer formed on the second SiO<sub>2</sub> layer.

In another embodiment of the present invention, the flash memory includes: a Si substrate; a first SiO<sub>2</sub> layer formed on the Si substrate; a first high- $\kappa$  layer formed on the first SiO<sub>2</sub> layer; a first HfON layer formed on the first high- $\kappa$  layer; a first Ge/oxynitride layer formed on the oxynitride layer; a second high- $\kappa$  layer formed on the Ge/oxynitride layer; a second SiO<sub>2</sub> layer formed on the second high- $\kappa$  layer; and a gate layer formed on the second SiO<sub>2</sub> layer.

The present invention further provides a method of fabricating a flash memory, including: providing a substrate; forming a first SiO<sub>2</sub> layer on the substrate; forming a first high- $\kappa$  layer on the first SiO<sub>2</sub> layer; forming a metal-implanted oxynitride layer on the first high- $\kappa$  layer; forming a second high- $\kappa$  layer on the metal-implanted oxynitride layer; forming a second SiO<sub>2</sub> layer on the second high- $\kappa$  layer; and forming a TaN layer on the second SiO<sub>2</sub> layer.

In an embodiment, the As-implanted ZrON is formed by implanting ZrON with As at 60°-tilted angle, 3 KeV and  $5 \times 10^{15}$  cm<sup>-2</sup> dose, and followed by 950° C. RTA.

## BRIEF DESCRIPTION OF DRAWINGS

The invention can be more fully understood by reading the following detailed description of the preferred embodiments, with reference made to the accompanying drawings, wherein:

FIGS. 1(a) to (c) are schematic band diagrams of a traditional MONOS CTF, a double Si<sub>3</sub>N<sub>4</sub>—HfON trapping CTF, and a As<sup>+</sup>-implanted ZrON CTF, respectively;

FIG. 2 shows  $J_g-V_g$  curves of ZrON MONOS nonvolatile memory (NVM) devices with and without As<sup>+</sup>-implant;

FIG. 3 shows C-V hysteresis of ZrON MONOS NVM devices with and without As<sup>+</sup>-implant;

FIG. 4 shows program characteristics of control ZrON MONOS NVM devices for different voltages and times;

FIG. 5 shows erase characteristics of control ZrON MONOS NVM devices for different voltages and times;

FIG. 6 shows program characteristics of As<sup>+</sup>-implanted ZrON MONOS NVM devices for different voltages and times;

FIG. 7 shows erase characteristics of As<sup>+</sup>-implanted ZrON MONOS NVM devices for different voltages and times;

FIG. 8 is a schematic structure of an As<sup>+</sup>-implanted ZrON/LaAlO<sub>3</sub>/SiO<sub>2</sub>/Si of an embodiment according to the present invention;

FIG. 9 shows XRD of control and As<sup>+</sup>-implanted ZrON/LaAlO<sub>3</sub>/SiO<sub>2</sub>/Si structure after 950° C. RTA;

FIG. 10 shows SIMS of the As<sup>+</sup>-implanted ZrON/LaAlO<sub>3</sub>/SiO<sub>2</sub>/Si structure after 950° C. RTA;

FIG. 11 shows retention characteristics of control un-implanted ZrON MONOS NVM devices at 25-125° C.;

FIG. 12 shows retention characteristics of As<sup>+</sup>-implanted ZrON MONOS NVM devices at 25-125° C.;

FIG. 13 shows endurance characteristics of As<sup>+</sup>-implanted ZrON MONOS NVM devices;

FIGS. 14(a) and (b) are a schematic structure and schematic energy band diagram of a Ge/HfON CTF memory of an embodiment according to the present invention, respectively;

FIGS. 15(a) and (b) show program and erase characteristics of HfON CTF memory with and without Ge for different voltages and times; and

FIGS. 16(a) and (b) show retention characteristics of a flash memory and cycling characteristics of HfON CTF memory with and without Ge.

## DETAILED DESCRIPTION OF THE INVENTION

The following illustrative embodiments are provided to illustrate the disclosure of the present invention, these and other advantages and effects can be apparently understood by those in the art after reading the disclosure of this specification. The present invention can also be performed or applied by other different embodiments. The details of the specification may be on the basis of different points and applications, and numerous modifications and variations can be devised without departing from the spirit of the present invention.

High performance MONOS CTF with highly scaled 3.6 nm ENT is reached and meets ITRS scaling target for the first time. At 125° C. and  $\pm 16$  V program/erase (P/E), the device has fast 100  $\mu$ s speed and large extrapolated 10-year retention of 3.1 V. The excellent results were reached using metallic Arsenic (As) implant into higher  $\kappa$  ZrON ( $\kappa=35$ ) as trapping layer. In contrast, small 10-year retention window of 1.9 V is found in control ZrON CTF. The improved memory window is due to the better electron trapping capability of As<sup>+</sup>-implanted ZrON. The excellent 10<sup>6</sup> cycles and good 125° C. retention may be ascribed to the deep  $E_{vac}-E_C$  ZrON and 5.1 eV work-function ( $\Phi_m$ ) of metallic As, to minimize the Schottky emission and tunnel leakage. The excellent 10<sup>6</sup> cycles are vitally important to allow further endurance improvement in highly scaled CTF device with fewer electrons. These results compare well with other reported data listed in Table 1, with

the smallest 3.6 nm ENT, fast 100  $\mu$ s speed, large memory window, good retention at 125° C. and the best 10<sup>6</sup> endurance.

TABLE 1

	P/E conditions for retention & cycling	Initial $\Delta V_{th}$ (V)	$\Delta V_{th}$ (V) for 10-year retention @85° C.	$\Delta V_{th}$ (V) for 10-year retention @125° C.	$\Delta V_{th}$ (V) @Cycles
This work (As <sup>+</sup> -implanted)	16V 100 $\mu$ s/-16 V 100 $\mu$ s	4.9	3.4	3.1	4.3@10 <sup>6</sup>
This work (control un-implanted)	16V 100 $\mu$ s/-16 V 100 $\mu$ s	2.9	2.1	1.9	—
TANOS	13.5 V 100 $\mu$ s/-13 V 10 ms	4.4	2.07	—	4@10 <sup>5</sup>
SiO <sub>2</sub> /Si <sub>3</sub> N <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub> /TaN Tri-gate	11.5 V 3 ms/-11.5 V 100 ms	1.2	1.1 (@25° C.)	—	1.5@10 <sup>4</sup>
SiO <sub>2</sub> /Si <sub>3</sub> N <sub>4</sub> /SiO <sub>2</sub> FinFET	13 V 10 $\mu$ s/-12 V 1 ms	4.5	2.4	—	3.5@10 <sup>4</sup>
SiO <sub>2</sub> /Si <sub>3</sub> N <sub>4</sub> /SiO <sub>2</sub> SiO <sub>2</sub> /AlGaIn/AlLaO <sub>3</sub>	11 V 100 $\mu$ s/-11 V 100 $\mu$ s	3.0	1.6	—	2.3@10 <sup>5</sup>

The TaN—[SiO<sub>2</sub>—LaAlO<sub>3</sub>]  
—ZrON—[LaAlO<sub>3</sub>—  
SiO<sub>2</sub>]  
—Si CTF device has 2.5 nm thermal SiO<sub>2</sub>, 2.5 nm  
LaAlO<sub>3</sub>, 18 nm ZrON<sub>0.2</sub>, 8 nm LaAlO<sub>3</sub>, 6 nm LPCVD SiO<sub>2</sub>,  
and 200 nm TaN. The LaAlO<sub>3</sub>, ZrON<sub>0.2</sub>, and TaN were depos-  
ited by physical vapor deposition (PVD). To improve the  
trapping capability, the ZrON was implanted by As at 60°-  
tilted angle, 3 KeV and 5×10<sup>15</sup> cm<sup>-2</sup> dose, followed by 950°  
C. RTA to reduce the ion-implanted damage. After gate defi-  
nition, self-aligned As<sup>+</sup> implant is applied and RTA is used  
to activate the dopants. The LaAlO<sub>3</sub> was from binary Al<sub>2</sub>O<sub>3</sub> and  
La<sub>2</sub>O<sub>3</sub>, used for V<sub>t</sub> tuning in 32 nm gate-first high- $\kappa$  p- and  
n-MOSFETs, respectively. For comparison, control CTF  
device was also fabricated without the As<sup>+</sup>-implant into  
ZrON.

#### A. P/E Characteristics:

FIG. 1 shows the traditional, double trapping Si<sub>3</sub>N<sub>4</sub>—  
HfON, and As<sup>+</sup>-implanted ZrON MONOS CTF devices. The  
As<sup>+</sup>-implanted ZrON has higher  $\kappa$  than HfON and deep  $\Phi_m$  of  
As for trapping. FIG. 2 shows the gate current (J<sub>g</sub>) of CTF.  
Close J<sub>g</sub> of As<sup>+</sup>-implanted device with control is reached.  
Larger C-V hysteresis of 8.1 V was obtained in As<sup>+</sup>-implanted  
CTF than control device under  $\pm$ 16 V sweep (FIG. 3). FIGS.  
4 and 5 show the program and erase data in control devices. A  
small  $\Delta V_{th}$  memory window of 2.9 V was measured at 100  $\mu$ s  
at  $\pm$ 16 V P/E that is typical for metal-oxide-nitride trapping  
MONOS with low trapping efficiency. The  $\Delta V_{th}$  is signifi-  
cantly larger for As<sup>+</sup>-implanted CTF devices shown in FIGS.  
6 and 7, with a large  $\Delta V_{th}$  window of 4.9 V at  $\pm$ 16 V 100  $\mu$ s  
P/E. This indicates the better trapping efficiency in As<sup>+</sup>-  
implanted ZrON that may be due to metallic As atoms and  
implant-created defects. Since a 950° C. RTA is applied to  
lower the implanted defects, the As atoms may play a major  
role for better trapping. The fast 100  $\mu$ s P/E speed is due to the  
existing  $\Delta E_C$  and  $\Delta E_V$  in LaAlO<sub>3</sub>/SiO<sub>2</sub> for easier tunneling,  
where the larger physical thickness improves the retention  
with only 3 nm EOT in tunnel oxide.

#### B. Characterization of As<sup>+</sup>-Implanted ZrON:

The As<sup>+</sup>-implanted ZrON has a schematic structure shown  
in FIG. 8, which was analyzed by XRD and SIMS shown in  
FIGS. 9 and 10. As shown in FIG. 8, a flash memory 10 of an  
embodiment according to the present invention comprises a  
substrate 102, a SiO<sub>2</sub> layer 104 formed on the substrate 102,  
a LaAlO<sub>3</sub> layer 106 formed on the SiO<sub>2</sub> layer 104, an As-  
implanted ZrON layer 108 formed on the LaAlO<sub>3</sub> layer 106,  
another LaAlO<sub>3</sub> layer 110 formed on the As-implanted ZrON  
layer 108, another SiO<sub>2</sub> layer 112 formed on the another  
LaAlO<sub>3</sub> layer 110, and a TaN layer 114 formed on the another

SiO<sub>2</sub> layer 112. In an embodiment, the SiO<sub>2</sub> layer 104 is 2.5  
nm thick; the LaAlO<sub>3</sub> layer 106 is 2.5 nm thick; the As-

implanted ZrON layer 108 is 18 nm thick; the another LaAlO<sub>3</sub>  
layer 110 is 8 nm thick; the another SiO<sub>2</sub> layer 112 is 6 nm  
thick; and the TaN layer 114 is 200 nm thick. The ZrON  
poly-grains are found in X-TEM that gives the higher  $\kappa$  value  
and smaller ENT. The XRD shows weak As peaks with the  
same angle of clustered As-dots in As-rich GaAs, which  
suggests the forming small As metal dots in ZrON although  
beyond our TEM resolution. Such metallic As with deep 5.1  
eV  $\Phi_m$  inside ZrON traps may also reduce the Schottky emis-  
sion and tunnel leakage, in addition to the large E<sub>vac</sub>-E<sub>C</sub> of  
ZrON. From SIMS, the As concentration at 60° 3-keV  
implant reduces rapidly with thickness and mainly within  
ZrON that explains the close J<sub>g</sub> with control device in FIG. 2.  
C. Retention & Endurance:

FIGS. 11 and 12 show the retention data of As<sup>+</sup>-implanted  
and control ZrON CTF devices at 25, 85 and 125° C. A large  
10-year extrapolated window of 3.1 V is measured at 125° C.  
in As<sup>+</sup>-implanted devices at 100  $\mu$ s and  $\pm$ 16 V P/E. This is  
significantly better than the 1.9 V 10-year window in control  
devices. Such large 10-year retention data allows multi-level  
cells (MLC) storage even at 125° C. The good retention is due  
to the extra  $\Delta E_C$  confinement energy in LaAlO<sub>3</sub>/ZrON/  
LaAlO<sub>3</sub> and also deep  $\Phi_m$  of metallic As shown in FIG. 1(c),  
while fast 100  $\mu$ s erase is also reached from the lowered hole  
energy barrier  $\Delta E_V$  in LaAlO<sub>3</sub>/SiO<sub>2</sub> tunnel oxide. The fast P/E  
speed and lowered hole tunnel barrier  $\Delta E_V$  lead to excellent  
endurance: as shown in FIG. 13, a still large 4.3 V window is  
obtained even at 10<sup>6</sup> P/E cycles. Such excellent cycling data  
are vitally important and allow further improving the endur-  
ance in highly scaled CTF device with fewer stored electrons.  
Table 1 compares various MONOS CTF devices. The novel  
device compares well with other devices, with the record  
thinnest 3.6 nm ENT trapping layer, large memory window,  
good 125° C. retention, fast 100  $\mu$ s P/E speed, and the highest  
10<sup>6</sup> endurance.

Using low energy As<sup>+</sup>-implant into higher  $\kappa$  ZrON trap-  
ping layer, this novel CTF device shows excellent device  
performance of highly scaled 3.6 nm ENT, large 10-year  
extrapolated retention window of 3.1 V at 125° C. and 1  
million times endurance, at a fast 100  $\mu$ s and low  $\pm$ 16V P/E.

Among various types of NVM, the flash memory has irre-  
placeable merits of the lowest switching energy and excellent  
device distribution that are vital for high-density sub-Tb  
memory arrays. To continue downscale into sub-20-nm, the  
MONOS CTF devices are proposed to replace the poly-Si  
floating-gate (FG) flash memory according to ITRS. This is  
due to the discrete charge-trapping property, simple planar



TABLE 2-continued

	NAND Flash poly $\frac{1}{2}$ Pitch (nm)					
	16	14	13	12	11	9
material						
Tunnel dielectric thickness	3-4	3-4	3-4	3-4	3-4	3-4
EOT (nm)						
Blocking dielectric material	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
Blocking dielectric thickness	6	5	5	5	5	5
EOT (nm)						
Charge trapping layer material	SiN/High-K	SiN/High-K	SiN/High-K	SiN/High-K	SiN/High-K	SiN/High-K
Charge trapping layer thickness (nm)	4-6	4-6	4-6	4-6	3-4	3-4
Gate material	Metal	Metal	Metal	Metal	Metal	Metal
Highest W/E voltage (V)	15-17	15-17	15-17	15-17	15-17	15-17
Endurance (erase/write cycles)	1.00E+04	1.00E+04	1.00E+04	1.00E+04	1.00E+04	1.00E+04
Nonvolatile data retention (years)	5-10	5-10	5-10	5-10	5-10	5-10
Maximum number of bits per cell (MLC)	4	4	4	4	4	4

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The foregoing descriptions of the detailed embodiments are only illustrated to disclose the features and functions of the present invention and not restrictive of the scope of the present invention. It should be understood to those in the art that all modifications and variations according to the spirit and principle in the disclosure of the present invention should fall within the scope of the appended claims.

What is claimed is:

1. A flash memory, comprising:
  - a substrate;
  - a first SiO<sub>2</sub> layer formed on the substrate;
  - a first high- $\kappa$  layer formed on the first SiO<sub>2</sub> layer;
  - an As-implanted metal oxynitride layer formed on the first high- $\kappa$  layer;
  - a second high- $\kappa$  layer formed on the metal-implanted metal oxynitride layer;
  - a second SiO<sub>2</sub> layer formed on the second high- $\kappa$  layer; and
  - a gate layer formed on the second SiO<sub>2</sub> layer.
2. The flash memory of claim 1, wherein the high- $\kappa$  layer is made of a first material of Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> or SiN or a ternary or quaternary combination of the first material, the metal oxynitride layer is made of a second material of AlON, LaON, HfON, ZrON, TiON or SiON or a quaternary combination of the second material.
3. The flash memory of claim 1, wherein the gate layer is made of metal or metal-nitride.
4. The flash memory of claim 3, wherein the metal-nitride is TiN, TaN or MoN.
5. A flash memory, comprising:
  - a Si substrate;
  - a first SiO<sub>2</sub> layer formed on the Si substrate;

- a first high- $\kappa$  layer formed on the first SiO<sub>2</sub> layer;
- a first oxynitride layer formed on the first high- $\kappa$  layer;
- a layer of oxynitride formed on the first oxynitride layer, wherein the oxynitride has a first metal and a second metal, and the first metal is hafnium;
- a second high- $\kappa$  layer formed on the layer of oxynitride;
- a second SiO<sub>2</sub> layer formed on the second high- $\kappa$  layer; and
- a gate layer formed on the second SiO<sub>2</sub> layer.
6. The flash memory of claim 5, further comprising:
  - a second oxynitride layer formed on the layer of oxynitride; and
  - a layer of oxynitride having a third metal formed on the second oxynitride layer,
 wherein the second high- $\kappa$  layer is directly formed on the layer of oxynitride having the third metal.
7. The flash memory of claim 6, wherein the high- $\kappa$  layer is made of a first material of Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> or SiN or a ternary or quaternary combination of the first material, the second metal oxynitride layer is made of a second material of AlON, LaON, HfON, ZrON, TiON or SiON or a quaternary combination of the second material, the first metal is As, Sb, Ga, or In, and the third metal is As, Sb, Ga, or In.
8. The flash memory of claim 5, wherein the gate layer is made of metal or metal-nitride.
9. The flash memory of claim 8, wherein the metal-nitride is TiN, TaN or MoN.
10. The flash memory claim 1, wherein the As-implanted metal oxynitride layer is an As-implanted HfON layer.

11. The flash memory of claim 5, wherein the layer of oxynitride having the first metal and the second metal is a HfGeON layer.

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