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Critical Issues of New Gate Insulator/Si Interfaces in the Future ULSI

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Critical issues in new ternary Gate oxide materials were discussed in terms of empirical glass theory, thermal stability, and interface reactions. To optimize the composition, the combinatorial synthesis and high throughput characterization were applied.
Key words: Gate insulator, oxide, combinatorial, and LSI

1. INTRODUCTION

The modern ULSI is standing at the critical edge from the materials aspects [1]. In the past four decade, the basic materials in ULSI as well as in IC have not change. They were typically Si, SiO_2 and Al. As the Gate insulator, SiO_2 has been used because SiO_2 is obtained simply by thermal reaction with Si and oxygen. The SiO_2/Si interface has been providing an ideal interface with atomically flatness, stable amorphous structure, and lower interface states. Recently due to the increasing number of transistors and decreasing the size of MOSFET, the thickness of the Gate insulator becomes 2 nm, where the tunneling current begins to increase from Gate to Drain [2]. To suppress the leakage current, the thickness of the Gate insulator must be increased, leading to the replacement of SiO_2 to a higher dielectric material [3]. This issue is expressed as a term of "High-k" problem. However it is not easy to find a new Gate insulator because of various requirements for the new materials.

In this paper, The requirements for the new dielectric material are reviewed and some candidates are discussed. Finally, as a discovery tools to find the new materials, the combinatorial synthesis and high through put characterizations are introduced.

2. REQUIREMENT FOR Gate INSULATOR

There are three major criteria in selecting the new Gate insular. They are structure factor, dielectric property and thermal stability with Si. It must be amorphous and should have higher dielectric property (higher than that of SiO_2) and should have abrupt interface with Si [2].

2.1 How to find amorphous oxides

Basically oxide materials are categorized into 3 groups[3,4]. One is the network forming oxides. This oxide can be amorphous for itself. SiO_2 is the typical one and Al_2O_3 is also involved in this group. Another one is the modifier oxide, which can be amorphous with a support of network forming oxide. Rare earth metal oxides, such as La_2O_3 or Pr_2O_3, are in this group. The last one is the intermediate oxide, which has a trend to be crystalline and it can only be amorphous with a simultaneous mixing with network forming oxide and modifier. As the Gate insulator, HfO_2 and ZrO_2 have been the leading candidates because of their higher dielectric properties. However two materials are involved in the intermediate oxide. For making the HfO_2 or ZrO_2 to be stable amorphous, simultaneous mixing with network forming oxide and intermediate ones is required. This means that a ternary alloying is inevitable for ZrO_2 or HfO_2 based alloy to be amorphous. Table I shows the categorized oxides.
From this table, for example, Al_2O_3 is listed as a network forming oxide and Y_2O_3 is shown as the modifier oxide.

Table I Categories of oxides
Oxides are categorized in three kinds of oxides.

network Former	Intermediate	modifier
SiO_2	TiO_2	La_2O_3
Al_2O_3	ZnO	Y_2O_3
GeO_2	PbO	SnO_2
B_2O_3	ThO_2	Ga_2O_3
P_2O_3	BeO	In_2O_3
V_2O_5	ZrO_2	BaO
As_2O_5	(HfO_2)	SrO
Sb_2O_5	CdO	Sc_2O_3
		ThO_2
		HgO

2.2 Thermal stability on Si

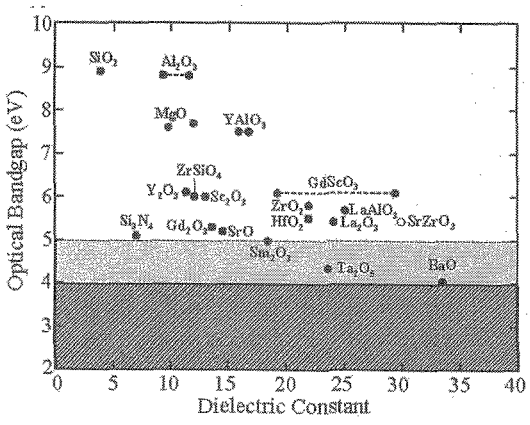
The interface between Gate insulator and Si is expected to be abrupt. However, from the results on thermodynamics calculation, most of oxides react with Si, forming SiO_2 or silicate at the interface[5]. Exceptionally ZrO_2 and HfO_2 are concluded that they can exist on Si without reaction layer, Other mixed oxides must be satisfy this condition to form abrupt

interfaces. SiO_2 and Al_2O_3 are known to have abrupt interfaces. Y_2O_3 and SrO, which are in the modifier oxide group, are also the candidate of less reaction with Si.

2.3 Electric structure of Gate insulator and band offset on Si

In selecting a new Gate dielectric oxide, the band offset of the oxide on Si is also the critical. Typically oxides which have higher dielectric property are transition metal oxides and the band gap of the oxides are determined by the energy gap between d orbital state and upper level of the valence band originated by s orbital of oxygen. The d state energy level affects to the Fermi level of the oxide, giving influence to the band offset as well as the dielectric property. In general, oxides which have higher dielectric property have narrow band gap and smaller band offset to Si[6]. $SrTiO_3$ is an example for this kind of oxide. From this aspect, HfO_2 and ZrO_2 are preferable and SrO and Y_2O_3 have enough values as the band offset. As SiO_2 and Al_2O_3 have no d-state electron, the band gaps are determined by the energy gap between s state of Si (or Al) and p state of oxygen. Therfore the band gaps are rather higher than those of transition metal oxide and give satisfactory band offset [6]. This trend is summarized in Table II.

Table II Relation between dielectric constant and Band Ga[6].
There are proper oxides which have higher dielectric constant and band gap. These are explained by electric structures of oxides.



2.4 Combinatorial synthesis and high throughput characterization

From a discussion in 2.1 to 2.3, for making HfO_2 or ZrO_2 to be stable amorphous oxide with abrupt interface as the practical Gate insulator, simultaneous mixing with Al_2O_3 and Y_2O_3 worth challenging, the problem, however, is how to optimize the composition of the ternary alloy of oxides. For this purpose, we have been proposing a "ternary combinatorial synthesis" with a combination of the microwave microscope as the high throughput characterization tool for rapid dielectric evaluation. The ternary combinatorial synthesis is carried out by pulsed laser deposition using three targets. During the deposition, with the continuous movement of the mask, a composition spread of oxide is completed. With a combination of sample rotation at 0 degree, 120 degree, and 240 degree, a ternary alloyed composition spread film can be demonstrated. A schematic illustration is shown in Fig.1. The detail will be presented in elsewhere [7].

For the quick estimation of dielectric property of the ternary alloyed oxide, the microwave microscope is suitable because electrode preparation and electrically measurement are not necessary for this evaluation. By scanning a probe on a sample, which is connected to a microwave resonator, a mapping of dielectric distribution is obtained [8].

3. EXPERIMENTS

Si (100) with 100 ohm-cm was used as a substrate. After a conventional Si cleaning process, this substrate was set in a combinatorial system where the ternary alloying is possible as described. For the film growth, the pulsed laser ablation was used. Here HfO_2, Y_2O_3 and Al_2O_3 were mixed in compositionally gradient at 300 C at 10^{-5} Torr oxygen atmosphere. The dielectric property was characterized by microwave microscope and structure on each composition was measured by combinatorial X-ray diffractions[9]. Atomic structure of oxide/Si interfaces were observed by transmission electron microscopy (TEM) . The TEM specimen was fabricated by micro sampling method, which enabled us to make a TEM sample from the points of interests [10].

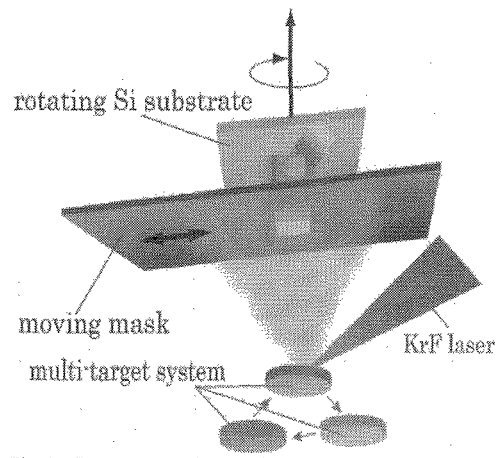
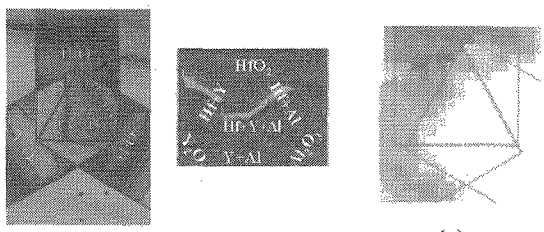


Fig.1 Schematic illustration of the combinatorial synthesis.
With a moving mask and sample rotation systems, a ternary alloy is formed.

4. RESULTS AND DISCUSSION

Fig.2 (a) shows a optical photo image of the HfO_2-Y_2O_3-Al_2O_3 ternary combinatorial sample. Clearly a ternary alloyed region was observed as a regular triangle in the center of the sample. Fig2 (b) shows the dielectric distribution of the sample measured by microwave microscope. Around HfO_2 region, higher dielectric area was observed, which is expressed as a dark contrast area. Fig2(c) shows the result of combinatorial X-ray diffraction measurement. At 300 C film growth, HfO_2 – Y_2O_3 regions were found to be poly

crystalline. However some regions which contained Al_2O_3 did show amorphous structure, which is expressed as a white region. With superimposing the results of dielectric property distribution and amorphous area, we found that the specific region (HfO_2:Y_2O_3:Al_2O_3=6:1:3) has a possibility of the required higher dielectric amorphous oxide [11]. From the TEM structure analysis, the region was assured to have an amorphous structure in atomic level. Fig. 3 shows the TEM image of the oxide/Si interface. In the films region, clearly a amorphous structure was observed. However at the oxide/Si interface, 0.4 nm



(a) (b) (c)

Fig.2 Combinatorial synthesis and high throughput characterizations.
Fi2 (a) shows a optical image of the combinatorial sample where HfO_2, Al_2O_3, and Y_2O_3 were mixed with composition spread method. In the center region, a ternary triangle is observed.
Fig.2(b) Dielectric mapping of the (a). Dark contrast region around HfO_2, indicates that the area has higher dielectric propery.
Fig.2(c) Structure mapping by combinatorial X-ray diffractions.
Colored regions are polycrystalline area. From the figure, HfO_2-Y_2O_3 has already crystallized. However, the region where $A_{l2}O3$ is involved, no X-ray peaks were observed, indicating the areas are amorphous.

SiO_2 or silicate region was observed. From the thermodynamic calculation, less reaction was expected. This contradiction is explained that the region was formed kinetically by oxygen diffusion during the film growth at the atmosphere of 10^{-5} Torr oxygen ambient.

5. CONCLUSION

To find a new Gate insulator, the required aspects were discussed in terms of empirical glass rule, thermal stability of oxide/Si interface, and electric structures of oxides. To optimize the composition, the combinatorial synthesis was employed as the film growth method. High throughput characterization by microwave microscope was also used to evaluate the dielectric property. From the results, the most appropriate composition was found in HfO_2-Y_2O_3:Al_2O_3 ternary alloy.

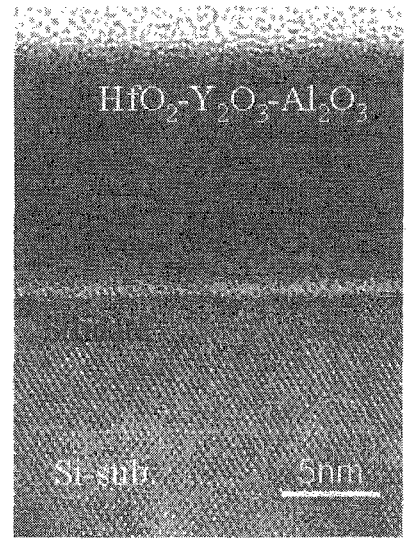


Fig.3 A high resolution transmission electron microscopy image of the oxide/Si interface.
In the oxide region, the observed structure was amorphous. However, at the interface region, SiO_2 or silicate layer of 0.4 nm was found. This interfacial layer was speculated to be formed kinetically by oxygen diffusion from the surface during the growth.

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