The development of sputtering method-used single-phase high dielectric constant non-SiO₂ gate dielectrics

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Abstract

In order to find the single-phase high dielectric FET gate-used ceramic materials, which will be used in the sputtering method and have the dielectric constants higher than that of SiO₂ and Si₃N₄, TiO₂, La₂O₃, and ZrO₂ are mixed with SiO₂ to format the (1-x) TiO₂-x SiO₂, (1-x) ZrO₂-x SiO₂, and (1-x) La₂O₃-x SiO₂ compositions. The all compositions are calcined at 1100°C and sintered at 1400°C~1550°C for 2h, and the X-ray patterns are used to find the crystal phases of all sintered ceramics. Because of the existence of single-phase, the sintering and dielectric characteristics of 0.3 La₂O₃-0.7 SiO₂ ceramic are further developed in this study.

Keywords: non-pure SiO₂ gate dielectric, high dielectric constant, X-ray, La₂Si₂O₇

1. Introduction

At 1999, the International Technology Roadmap for Semiconductors predicted the thickness of FET SiO₂ gate would be shortened from 2.5 nano-meter at 1999 to 1.0 nano-meter at 2005. Recently, the thickness of FET gate has been lowered down, 1.5 nano-meter SiO₂ gate for 0.1~0.12μm FET used has been well developed, but the problem for the fabrication of SiO₂ gate below 1.5 nano-meter has not been dissolved [1-3]. To dissolve this problem, the dielectric constant of gate-used dielectrics must be increased and the development of high dielectric constant not pure SiO₂ gate dielectrics is the important study topic. Using high dielectric constant dielectrics would be indispensable for the gate dielectrics of complementary metal oxide semiconductor field-effect transistors (CMOSFETs), particularly in low power applications, where conventional SiO₂ and Si₃N₄ dielectrics are unable to meet the gate leakage current specifications [1-3]. Many dielectric systems are currently under consideration as potential replacements for SiO₂ and Si₃N₄ as the gate dielectrics for CMOSFETs technology [4]. The required properties for the key guidelines of selecting an alternative gate dielectrics are (a) permittivity and band alignment to silicon, (b) thermodynamic stability, (c) easy film morphology, (d) high interface quality, (e) having the compatibility current ability to be used in processing for CMOS devices, (f) process compatibility, and (g) high reliability [5]. Many dielectrics appear favorable in some of these areas, especially for the non-pure SiO₂ dielectrics of TiO₂-SiO₂, ZrO₂-SiO₂, and La₂O₃-SiO₂ compositions [6-9]. In the past, the effects of crystal structures of TiO₂-SiO₂, ZrO₂-SiO₂, and La₂O₃-SiO₂ compositions were not well developed. We believe that if single phase can not be obtained, the fabricated non-SiO₂ gate dielectrics will not reveal the stable dielectric characteristics and the dielectric characteristics will be deviated as the fabrication process are changed. In this study, TiO₂, ZrO₂, La₂O₃, and SiO₂ were used as source materials to format (1-x) TiO₂-x SiO₂, (1-x) ZrO₂-x SiO₂, and (1-x) La₂O₃-x SiO₂ compositions by using solid state reaction method. The influences of sintering temperature and
compositions on the crystal structures and sintering characteristics of all compositions are developed, in order to find the single-phase compositions can be used as the target materials of sputtering method to fabricate non-SiO₂ gate dielectrics.

2. Experimental procedures

The ceramic materials (1-x) TiO₂-x SiO₂, (1-x) ZrO₂-x SiO₂, and (1-x) La₂O₃-x SiO₂ were prepared by the solid state reaction method. Reagent-grade raw materials of TiO₂, ZrO₂, La₂O₃, and SiO₂ with higher than 99.5% purity were used as starting materials, mixed according to the compositions (1-x) TiO₂-x SiO₂ (x=0.4, 0.5, and 0.6), (1-x) ZrO₂-x SiO₂ (x=0.5, 0.6, 0.7, and 0.8), and (1-x) La₂O₃-x SiO₂ (x=0.6, 0.7, and 0.8), respectively, and ball-milled for 5h with deionized water. After dried and ground, then the powders were calcined at 1100°C for 2h. After calcinations, the powders were ground again, then polyvinylalcohol (PVA) was added as a binder. The calcining powders were uniaxially pressed into pellets in a steel die with the size of 1mm in thick and 12mm in diameter. After debindering, sintering of these pellets was carried out from 1400°C to 1550°C for 2h. The crystal structures of (1-x) TiO₂-x SiO₂, (1-x) ZrO₂-x SiO₂, and (1-x) La₂O₃-x SiO₂ ceramics were investigated using XRD patterns. After the analysis, it is found that only the 0.3 La₂O₃-0.7 SiO₂ ceramics will reveal a single-phase structure of La₂Si₂O₇. For that the morphologies of 0.3 La₂O₃-0.7 SiO₂ ceramics were observed by using scanning electronic micrograph (SEM). The sintered 0.3 La₂O₃-0.7 SiO₂ ceramic were painted with Ag-Pd paste and sintered at 700°C for 15min. The dielectric characteristics of 0.3 La₂O₃-0.7 SiO₂ ceramic were measured at 1MHz with an oscillating amplitude (50mV) by an HP4194 impedance analyzer.

3. Results and discussion

Fig.1 shows the X-ray diffraction patterns of (1-x) TiO₂-x SiO₂ ceramics, as a function of sintering temperature and SiO₂ content. The crystal structures of (1-x) TiO₂-x SiO₂ ceramics are similar and independent of the sintering temperature and SiO₂ content. The X-ray analysis find that even 1550°C is used as the sintering temperatures, the (1-x) TiO₂-x SiO₂ compositions (x=0.4, 0.5, and 0.6) are not formatted a solid solution and the TiO₂ and SiO₂ exist as independent crystal phases. Using the crystal intensity of TiO₂ phase as index, the crystal intensity of SiO₂ increases with the increase of SiO₂ content and slightly decreases with the increase of sintering temperature.

Fig.2 shows the X-ray diffraction patterns of (1-x) ZrO₂-x SiO₂ ceramics, as a function of sintering temperature and SiO₂ content. The crystal phases of (1-x) ZrO₂-x SiO₂ ceramics are
different and dependent on the SiO₂ content. The solid solution would happen and the crystal phases of (1-x) ZrO₂-x SiO₂ compositions are very complicated. For x=0.5, the unknown phases are crystallized as main phase, ZrO₂, SiO₂, and ZrSiO₄ phase coexist; For x=0.6, the ZrSiO₄ is crystallized as main phase, ZrO₂, SiO₂, and the unknown phases are coexisted, and the crystal intensities of unknown phases decrease with the increase of sintering temperature. For x=0.7 and 0.8, SiO₂ crystals as main phase, ZrO₂, ZrSiO₄ phase, and the unknown phases coexist. For x=0.7, the crystal intensity of ZrSiO₄ phase critically increases with the increase of sintering temperature. As the sintering temperature increases from 1450°C to 1550°C and using SiO₂ as index, the crystal intensities of ZrSiO₄ increase and the crystal intensity of ZrO₂ decreases. However, the single-phase crystal structure is not found in the (1-x) ZrO₂-x SiO₂ compositions.

Fig.2 The X-ray diffraction patterns of (1-x) ZrO₂-x SiO₂ ceramics as a function of sintering temperature and SiO₂ content (x= 0.5, 0.6, 0.7 and 0.8).

The diffraction patterns of (1-x) La₂O₃-x SiO₂ ceramics are shown in Fig.3 as a function of sintering temperature and SiO₂ content. The crystal phases of (1-x) La₂O₃-x SiO₂ ceramics are different and dependent on the SiO₂ content. One single-phase solid solution of La₂Si₂O₇ is revealed in the 0.3 La₂O₃-0.7 SiO₂ composition, but complicated crystal phases are observed in the 0.6 La₂O₃-0.4 SiO₂ and 0.8 La₂O₃-0.2 SiO₂ compositions. For x=0.6, the La₉.₃₁(Si₁.₀₄O₄)₆O₂ and La₂Si₂O₇ phases exist as two different phases; For x=0.8, the La₂Si₂O₇ phase is coexisted with the SiO₂ phase. Using La₉.₃₁(Si₁.₀₄O₄)₆O₂ as index, the crystal intensities of La₂Si₂O₇ and SiO₂ decrease with the increase of sintering temperature.

Fig.3 The X-ray diffraction patterns of (1-x) La₂O₃-x SiO₂ ceramics, as a function of sintering temperature and SiO₂ content (x= 0.6, 0.7 and 0.8).

As Figs.1-3 show, if the compositions are not formatted a single-phase dielectric, the crystal intensities of formatted phases are changed as the SiO₂ content and sintering temperature increase, and it is believed the dielectric characteristics will also be changed. These results prove that formatted a single-phase dielectric would be the important topic to find a dielectric as a non-SiO₂
gate dielectric. Because of the existence of single-phase of La$_2$Si$_2$O$_7$, the sintering and dielectric characteristics of the 0.3 La$_2$O$_3$-0.7 SiO$_2$ ceramics are further developed in this study. From the micrographs observation of Fig.4, it is found that the 0.3 La$_2$O$_3$-0.7 SiO$_2$ (La$_2$Si$_2$O$_7$) ceramics can be densified at about 1450°C even the pores are still observed. From the results shown in Fig.5, the dielectric constant increases and the loss tangent decreases with the increase of sintering temperature, the decrease of pores will cause this result. The La$_2$Si$_2$O$_7$ ceramics have dielectric constant of 15~19, which is higher than that of SiO$_2$. And the loss tangent is in the range of 1.5~2.5%, which is lower enough for gate dielectric used. For that the La$_2$Si$_2$O$_7$ ceramics can be developed as the target of sputtering method to fabricate high dielectric constant gate dielectric.

![Image](image.png)

**Fig.4** The micrographs of 1450°C-sintered 0.3 La$_2$O$_3$-0.7 SiO$_2$ ceramics.

**Fig.5** The dielectric characteristics of 0.3 La$_2$O$_3$-0.7 SiO$_2$ ceramics.

### 4. Conclusions

The X-ray analysis find that the single-phase crystal structure is not found in the (1-x) TiO$_2$-x SiO$_2$ and (1-x) ZrO$_2$-x SiO$_2$ compositions. When the fabricated condition is changed, the dielectric characteristics will be different because of the deviation of crystal phases. The X-ray analysis find that one single-phase solid solution of La$_2$Si$_2$O$_7$ are observed in the 0.3 La$_2$O$_3$-0.7 SiO$_2$ composition, but complicated crystal phases are observed in the 0.6 La$_2$O$_3$-0.4 SiO$_2$ and 0.8 La$_2$O$_3$-0.2SiO$_2$ compositions. In the study, the 0.3 La$_2$O$_3$-0.7 SiO$_2$ has the single crystal phase of La$_2$Si$_2$O$_7$, higher dielectric constant, and lower dielectric loss, it is the optimum chose to be the sputter target source. This study also suggest as when the other method is used to fabricate the non-SiO$_2$ gate dielectrics, the 0.3 La$_2$O$_3$-0.7 SiO$_2$ composition would be a better choice.

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**References**