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Dielectric properties of sol–gel derived high-k titanium silicate thin films

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Abstract

High-k dielectric titanium silicate ($Ti_xSi_{1-x}O_2$) thin films have been deposited by means of an optimized sol–gel process. At the optimal firing temperature of 600 °C, the $Ti_{0.5}Si_{0.5}O_2$ films are shown to exhibit not only a dielectric constant (k) as high as ~23 but more importantly the lowest leakage current and dielectric losses. Fourier transform infrared spectroscopy shows an absorbance peak at 930 cm^{-1}, which is a clear signature of the formation of Ti–O–Si bondings in all the silicate films. The developed sol–gel process offers the required latitude to grow $Ti_xSi_{1-x}O_2$ with any composition (x) in the whole $0 \leq x \leq 1$ range. Thus, the k value of the $Ti_xSi_{1-x}O_2$ films can be tuned at any value between that of SiO_2 (3.8) to that of TiO_2 (k ~60) by simply controlling the TiO_2 content of the films. The composition dependence of the dielectric constant of the $Ti_xSi_{1-x}O_2$ films is analyzed in the light of existing models for dielectric composites.
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Keywords: Titanium silicate; High dielectric constant (High-k); Dielectric properties; Electrical properties and measurements; Sol–gel; Fourier transform infrared spectroscopy (FTIR)

1. Introduction

The continuing reduction in size of complementary metal-oxide-semiconductor (CMOS) devices and the increasing integration of CMOS components with microelectromechanical systems have put a severe demand on high-k materials with excellent electrical properties. Metal oxides were the first candidates that have been investigated for this purpose. However, it has been demonstrated that, while they can potentially offer high dielectric constants, they form an undesirable silicon dioxide layer at their interface with silicon, reducing thereby the effective dielectric constant [1,2]. Recently, metal silicates have been proposed as a choice better than the oxides because of the strong bonding of oxygen in the silicate compared to the metal oxide phases [3]. Nevertheless, as one would expect, a mixing of the metal oxide with the SiO_2, to form the metal silicate, would result in a dielectric constant of the silicate phase lower than that of the metal oxide. As an example, while metal oxides, such as ZrO_2 and HfO_2, are known to exhibit relatively high dielectric constant (k) of ~25, the k value of their silicate counterparts ($ZrSiO_4$ or $HfSiO_4$, respectively) are rather of ~11 [3]. In the literature, apart from mixing silicon dioxide with metal oxides, several studies have been also carried out to combine two different metal oxides to understand their resulting dielectric properties. For example, Ta_2O_5 has been mixed with TiO_2 [4], ZrO_2 [5] and NbO_2 [6] and their dielectric properties have been studied. Very recently, the structural and electric properties of TiO_2–HfO_2 have also been investigated [7].

Among the metal silicate family, titanium silicates ($Ti_xSi_{1-x}O_2$) are definitely one of the most promising high-k dielectric materials because of the highest k value of TiO_2 (i.e.; ~60 versus 25 for ZrO_2 and HfO_2, for example). The titanium silicates have been synthesized by means of various approaches including pulsed laser deposition [8–10], sputtering [11–13], chemical vapor deposition (CVD) [14], a photo induced CVD process [15], and sol–gel [16–18]. Most of the experimental work reported so far dealt with the understanding of the chemical, structural and optical properties of titanium silicate thin films. Surprisingly, only few experimental studies have been carried out on the investigation of the dielectric properties of these films [8–10,12,13]. In particular, we have recently demonstrated that an optimized reactive rf-magnetron sputtering process using an equi-atomic TiO_2–SiO_2 composite target produces titanium silicate thin films exhibiting a

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dielectric constant of ∼20. Nevertheless, it is highly desirable to develop high-*k* titanium silicate with more easy-to-implement, cost effective and batch-processing compatible methods, such as sol–gel processing. To this end, we have developed a sol–gel process for the spin coating of titanium silicate thin films. It is a fact that the sol–gel processing of titanium silicate films is quite challenging because of the considerable difference between the chemical characteristics of the Si and Ti precursors. Indeed, the hydrolysis rate and condensation rate for Si precursors $Si(OR)_4$ (5×10^{-19} and 1×10^{-14} $mol^{-1}s^{-1}$, respectively) are about five orders of magnitude lower than that of Ti precursors $Ti(OR)_4$ (1×10^{-13} and 30 $mol^{-1}s^{-1}$, respectively) [19].

In this paper, we first focus on the optimization of the firing temperature of the sol–gel derived $Ti_{0.5}Si_{0.5}O_2$ films. Secondly, we report on the effect of the composition of the $Ti_xSi_{1-x}O_2$ films on their dielectric properties. The developed process is shown to permit the control of the film composition (over the whole composition range: $0\leq x\leq1$), which, in turn, enables the tailoring of the dielectric properties of the $Ti_xSi_{1-x}O_2$ films. In particular, their dielectric constant can be fairly controlled at will over a range as wide as (3.8 to ∼60).

2. Experimental details

Tetrabutoxytitanium $[Ti(OC_4H_9)_4]$ (TBOT) and tetraethoxysilicon $[Si(OC_2H_5)_4]$ (TEOS) were used as precursors for the Ti and Si, respectively. Due to the difference of the hydrolysis rate, TEOS was activated at 70 °C for 2 h in a mixture of ethanol and 0.1 M HCl (in a volume ratio of 12:12:1 for TEOS, ethanol, and HCl respectively). Equal volume of TBOT and ethanol were also separately mixed and stirred for 3 min prior to its mixing with the TEOS activated sol. The composition of the films (i.e., *x* in $Ti_xSi_{1-x}O_2$) was controlled by the molar ratio of the TEOS and TBOT in the mixed sol. The mixed sol was stirred for 3 min and aged for 72 h before spin coating. A final dilution of the mixed sol with an equal volume of ethanol was performed prior to the spin coating to control the viscosity of the films. Thin films were spin coated at 4000 rpm for 30 s both on Si substrates as well as on Pt-coated Si substrates and dried at 120°C for 30 min. Then, the coated films were fired in an O_2 atmosphere at different temperatures (400 °C–800 °C) for 1 h. The atomic composition of the films was determined from X-ray photoelectron spectroscopy (XPS) spectra acquired by using the ESCALAB 220I-XL spectrophotometer. The bonding states of the films were systematically investigated by means of Fourier transform infrared (FTIR) spectroscopy, using a BOMEM-Michelson-100 spectrometer in the 350–4000 cm^{-1} range. For the characterization of the dielectric properties, the $Ti_xSi_{1-x}O_2$ films were integrated into metal–insulator–metal (MIM) devices (where Pt was used as bottom and top electrodes). The capacitance of the fabricated MIM devices was obtained from complex impedance (Z; $Z=1/Y$, where Y is the complex admittance) measurements, performed in the 0.1 kHz–10 MHz frequency (f) range, using an HP4192A LF impedance analyzer. The capacitance (C) and dissipation factor ($\tan(\delta)$) of the MIMs are respectively given by: $C=\mathrm{Im}(Y)/2\pi f$ and $\tan(\delta)=\mathrm{Re}(Y)/\mathrm{Im}(Y)$, where Im and Re refers to the imaginary and real parts of Y. The dielectric constant (k) of the films was then derived from the parallel-plate capacitor formula (i.e.; $C=(k\epsilon_0A)/d$, where A is the top electrode area and d the thickness of the film). The current–voltage (I–V) characteristics were collected using an HP4140B pA meter. The thickness of the films was determined through cross-section scanning electron microscopy

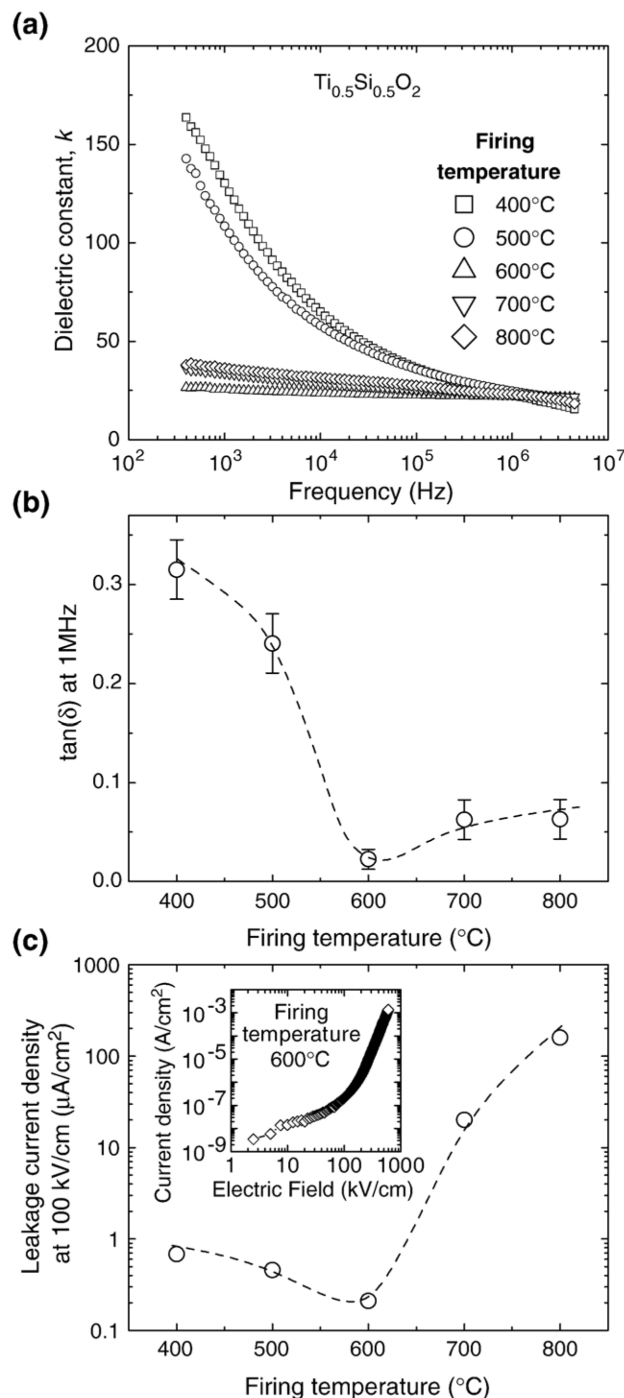

Fig. 1. (a) Variation of dielectric constant (k) with frequency for various firing temperatures of $Ti_{0.5}Si_{0.5}O_2$ samples, (b) firing temperature dependence of the dissipation factor $\tan(\delta)$, and (c) firing temperature dependence of the leakage current density of the $Ti_{0.5}Si_{0.5}O_2$ films. Inset of (c) shows a typical leakage current density *vs.* electric field for $Ti_{0.5}Si_{0.5}O_2$ films fired at 600 °C.

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