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Structural properties and electrical characteristics of high-k $Tm_2Ti_2O_7$ gate dielectrics

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ABSTRACT

In this article, the structural and electrical characteristics of high-k $Tm_2Ti_2O_7$ gate dielectrics deposited on Si (1 0 0) by means of reactive cosputtering were reported. The $Tm_2Ti_2O_7$ dielectrics annealed at 800 °C exhibited excellent electrical properties such as high capacitance value, small density of interface state, almost no hysteresis voltage, and low leakage current. This phenomenon is attributed to a rather well-crystallized $Tm_2Ti_2O_7$ structure and composition and a smooth surface observed by X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy, respectively. This film also shows almost negligible charge trapping under high constant voltage stress.

1. Introduction

The scaling rule to a metal-oxide-semiconductor field effect transistor (MOSFET) involves a reduction in the thickness of the gate dielectric. However, a high tunnelling current is generated when the gate dielectric thickness is less than 2 nm. To suppress the direct tunnelling current, a high-k dielectric material with a large film thickness achieves the same capacitance as that of a MOSFET with a thinner SiO_2 [1]. Lanthanide series rare-earth (RE) oxides, such as, La_2O_3 [2], Pr_2O_3 [3], Dy_2O_3 [4], Er_2O_3 [5], and Tm_2O_3 [6], are being considered as alternative gate dielectrics for advanced semiconductor devices because of their high permittivities, large band gaps, large conduction band offsets, and thermodynamic stability with Si [7,8]. Paivasaari et al. demonstrated that the physical and electrical properties of Tm_2O_3 thin film were grown on Si (1 0 0) substrate by atomic layer deposition [9]. However, low permittivity was found in the RE film [10]. This is mainly due to the low density of amorphous RE films or the moisture absorption, resulting in the formation of low permittivity hydroxide after the exposure to an air ambient [11].

The incorporation of TiO_2 film into RE oxide has proven to be stable against moisture [12]. Moreover, van Dover [13] showed that the TiO_2 or Ti combined with RE oxide films has attracted much attention as a method to obtain a high-k dielectric material with excellent electrical properties in terms of a large dielectric constant, a high breakdown voltage, and a low leakage current. In this article, we reported the structural properties and electrical characteristics of high-k $Tm_2Ti_2O_7$ dielectrics deposited on Si substrate by reactive cosputtering. The film structure and composition were investigated by combining X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The surface roughness of $Tm_2Ti_2O_7$ dielectric films after annealing at different temperatures was characterized with atomic force microscopy (AFM). Moreover, the effects of postdeposition annealing (PDA) on the electrical properties were discussed.

2. Experimental

Metal-oxide-semiconductor (MOS) devices fabricating $Tm_2Ti_2O_7$ dielectric films were deposited on 4 in. p-type Si (1 0 0) substrates. Prior to deposition of $Tm_2Ti_2O_7$ film, the Si wafers were cleaned by a traditional RCA process and then dipped in dilute HF for 30 s to remove the chemical oxide from the Si surface. A ~15 nm $Tm_2Ti_2O_7$ film was deposited on the Si substrate by rf cosputtering Tm and Ti from a pure thulium target (99.9%) and pure titanium target (99.9%) in diluted O_2 ambient (Ar/O_2 = 5 sccm/2 sccm) at substrate temperature of 27 °C. The base pressure in the sputtering system was about 1×10^{-6} Torr, the growth rate of the film was 0.6 Å/s, and the distance of the target to substrate was 15 cm. During deposition the total pressure was maintained at $\sim 10^{-3}$ Torr. Samples were then annealed at different temperatures in O_2 gas (500 Torr) for 30 s by rapid thermal annealing (RTA) to form a $Tm_2Ti_2O_7$ compound. A 1000 Å TiN film was deposited on the $Tm_2Ti_2O_7$ by sputtering to serve as the gate electrode. The capacitor area of 3.14×10^{-4} cm^2 was defined by photolithography and wet etching. Finally, a 4000 Å Al film was deposited on the back-side contact of the Si wafer.

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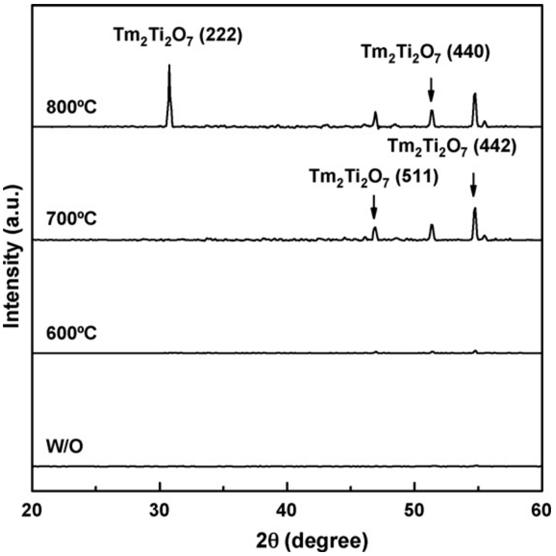

Fig. 1. XRD of $Tm_2Ti_2O_7$ dielectric films after annealing at various temperatures.

The thicknesses of $Tm_2Ti_2O_7$ thin films were determined using spectroscopic ellipsometry. The film structure and composition were investigated by XRD and XPS, respectively. The surface morphologies of the films were examined by AFM. The high-frequency (100 kHz) capacitance–voltage (*C*–*V*) measurement was made using a Hewlett-Packard (HP) 4285A inductance-capacitance-resistance meter. The capacitance equivalent thickness (CET) of the samples was estimated from the *C*–*V* curves. The electrical characteristics of the MOS capacitors were measured by using the HP 4156C semiconductor parameter analyser.

3. Results and discussion

The XRD patterns of $Tm_2Ti_2O_7$ films after PDA at various temperatures are presented in Fig. 1. In the as-deposited sample, no peak was found in the XRD pattern, suggesting an amorphous nature for this sample. Additionally, no peak was also observed in the 600 °C-annealed film. Two small ((5 1 1) and (4 4 0)) peaks and one strong (4 4 2) peak were found in the 700 °C-annealed sample. One stronger peak (2 2 2) and three weaker ((5 1 1), (4 4 0), and (4 4 2)) peaks were found in the analyzed 2θ range for the 800 °C-annealed sample, indicative of a rather well-crystallized $Tm_2Ti_2O_7$. This suggests a preferential orientation of the crystallites with the (1 1 1) planes of cubic $Tm_2Ti_2O_7$ parallel to the substrate.

Fig. 2 shows the Tm 4d, Ti 2p, and O 1s XPS spectra for the $Tm_2Ti_2O_7$ film before and after RTA treatment. Oxygen bonding to thulium and titanium is expected to shift the Tm 4d peak toward higher binding energies (177 eV corresponding to $Tm_2Ti_2O_7$) as compared to Tm–O (175.6 eV corresponding to Tm_2O_3) in Tm_2O_3 by considering the coordination number of titanium [14]. The Tm 4d peak position of the film after RTA at 700 °C shifts to a higher binding energy by about 1 eV relative to the Tm_2O_3 position, suggesting Tm atom reaction with Si resulting in a Tm silicate layer. After annealing performed at 800 °C, the Tm 4d peak at 177 eV with respect to $Tm_2Ti_2O_7$ bonds present in the film is shown in Fig. 2(a). The Ti 2p doublet (Ti $2p_{1/2}$ and Ti $2p_{3/2}$ at 465.8 and 459.9 eV, respectively) is shifted to higher binding energy compared to the TiO_2 reference position (Ti $2p_{1/2}$ and Ti $2p_{3/2}$ at 464.3 and 458.7 eV, respectively) [15], as shown in Fig. 2(b). This shift was attributed to Ti in $Tm_2Ti_2O_7$ compound. In addition, no evidence for Ti–Si bonds from silicides was observed on the Ti 2p spectra. The O 1s spectra in Fig. 2(c) can be deconvoluted to three chemical states. The low binding energy state at 529.7 eV can be related to O in Tm_2O_3 [16]. The median binding energy state at 530.9 eV can be attributed to O in $Tm_2Ti_2O_7$. The high binding energy state at 532.2 eV can be related to interfacial O atoms in nonstoichiometric Tm silicate. The as-deposited film seems to be composed mainly of Tm_2O_3, $Tm_2Ti_2O_7$ and silicate. The O 1s peak intensity corresponding to Tm_2O_3 is rather constant up to 600 °C but suddenly decreases at 700 °C, whereas the O 1s peak intensity corresponding to $Tm_2Ti_2O_7$ suddenly increases at 700 °C. This suggests that the oxygen moving from the $Tm_2Ti_2O_7$ film was mostly consumed by the formation of silicate. Moreover, the area and intensity of the O 1s peak at 530.9 eV corresponding to $Tm_2Ti_2O_7$ remain almost unaltered with high temperature annealing, indicating that a well-crystallized $Tm_2Ti_2O_7$ structure resulting in a higher thermal stability and a lower diffusivity of oxygen.

The postdeposition annealing in the film may influence the film roughness. Fig. 3 shows the surface roughness of $Tm_2Ti_2O_7$ films as a function of the RTA temperature. The surface roughness of $Tm_2Ti_2O_7$ film clearly decreases with increasing PDA temperature. This may be attributed to the film condensed during the annealing process. In addition, the availability of defect sites due to lower

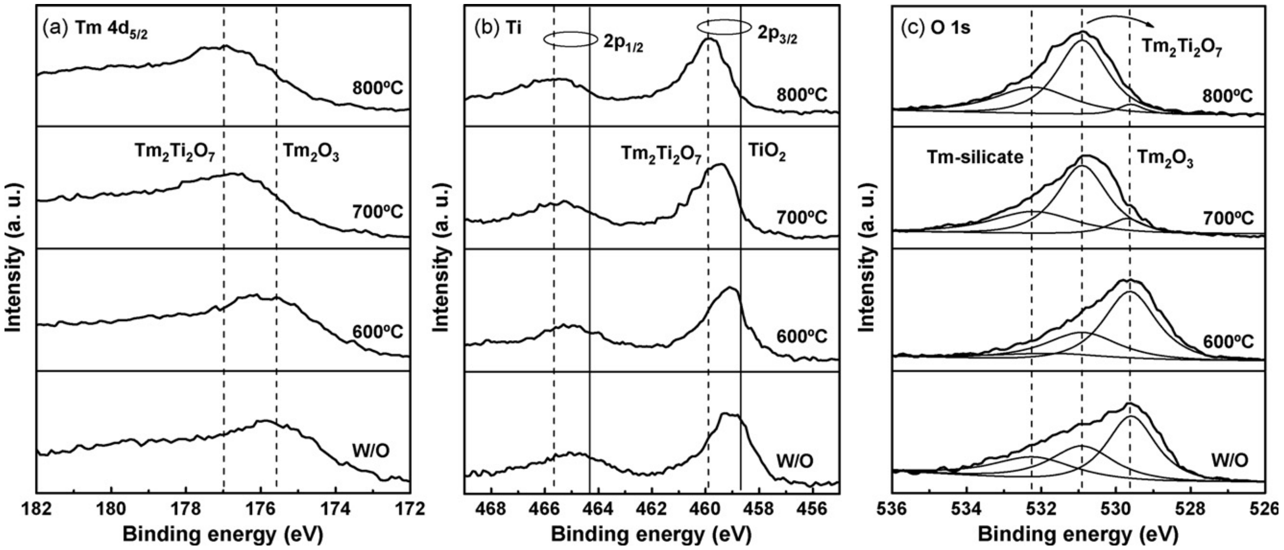

Fig. 2. XPS results of (a) Tm 4d, (b) Ti 2p, and (c) O 1s in $Tm_2Ti_2O_7$ film after annealing at various temperatures.