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Fabrication and characterization of La-doped HfO_2 gate dielectrics by metal-organic chemical vapor deposition

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ABSTRACT

La-doped HfO_2 gate dielectric thin films have been deposited on Si substrates using $La(acac)_3$ and $Hf(acac)_4$ (acac = 2,4-pentanedionate) mixing sources by low-pressure metal-organic chemical vapor deposition (MOCVD). The structure, thermal stability, and electrical properties of La-doped HfO_2 films have been investigated. Inductive coupled plasma analyses confirm that the La content ranging from 1 to 5 mol% is involved in the films. The films show smaller roughness of ~0.5 nm and improved thermal stability up to 750 °C. The La-doped HfO_2 films on Pt-coated Si and fused quartz substrates have an intrinsic dielectric constant of ~28 at 1 MHz and a band gap of 5.6 eV, respectively. X-ray photoelectron spectroscopy analyses reveal that the interfacial layer is Hf-based silicate. The reliable value of equivalent oxide thickness (EOT) around 1.2 nm has been obtained, but with a large leakage current density of 3 A/cm^2 at $V_g = 1V + V_{fb}$. MOCVD-derived La-doped HfO_2 is demonstrated to be a potential high-*k* gate dielectric film for next generation metal oxide semiconductor field effect transistor applications.

1. Introduction

High-*k* gate dielectrics are currently explored as an alternative gate dielectric material to replace conventional SiO_2 to solve the issues of device reliability and high gate leakage currents [1]. HfO_2 has been studied as one of the most promising high-*k* gate dielectrics for integration in complementary metal oxide semiconductor (CMOS) devices due to its high dielectric constant, wide band gap and good thermal stability on Si [2]. HfO_2 has been shown to crystallize at relatively low temperatures (~400 °C). However, it is preferable that gate insulators stay amorphous after a conventional activation annealing (800 °C) because it is a concern that grain boundaries may serve as the paths of dopant diffusion and produce a variation of electrical properties [3].

It is reported that La_2O_3 has a relatively wide band gap (5.5 eV) and a high dielectric constant ($k \sim 30$) and a high electron barrier to Si (2.3 eV) [2,4]. In addition, La_2O_3 is thermodynamically stable on Si [5]. However, it is important to note that pure La_2O_3 has been shown to absorb moisture readily when exposed to air [2,6]. Introducing La_2O_3 to HfO_2 nanophase powders can raise the crystallization temperature (800 °C) [7]. The increase in crystallization temperature relaxes the constraint on the maximum permissible dopant activation temperatures in the implementation of high-*k* dielectrics in metal oxide semiconductor field effect transistor (MOSFET) [8–11]. La_2O_3 will not cause the degradation of dielectric constant due to its higher dielectric constant than SiO_2 or Al_2O_3. Some groups have reported the characteristics of La-doped HfO_2 gate dielectrics prepared by sputtering deposition [3,7], atomic layer deposition (ALD) [12–15], liquid injection MOCVD [16], pulse laser deposition (PLD) [17,18] and molecular-beam epitaxy (MBE) [19–21]. La-doped HfO_2 exhibits promising thermodynamic and electrical properties for MOSFET applications.

Metal-organic chemical vapor deposition (MOCVD) is widely acknowledged as the most potential and competitive approach for high-*k* gate dielectrics due to its excellent compatibility with Si technology and high throughout [22–24]. In this paper, the La-doped HfO_2 films were deposited on Si substrates by MOCVD. The precursor has been used were $La(acac)_3$ (acac = 2,4-pentanedionate) and $Hf(acac)_4$. And the structure, thermal stability and electrical properties of La-doped HfO_2 films were investigated by means of a series of analytical techniques.

2. Experiment

La-doped HfO_2 oxide films were deposited using solid injector MOCVD. The metal-organic precursors used were $La(acac)_3$ and $Hf(acac)_4$ mixing sources. During every deposition process, some

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amount of La/Hf mixing sources (~0.5 g) was put in quartz boat for sublimation.

The substrates we used were 2–4 Ω cm n-type Si (1 0 0), fused quartz and Pt-coated Si, respectively. N-type Si was cleaned by a standard RCA technique to remove organic and metallic contaminants on the wafer surface. Then, the native silicon oxide layer on the surface was removed by immersing into a buffered HF solution ($HF:H_2O$ = 1:10, volume ratio) for 3 min and followed by rinsing in deionized water for 3 min. Finally, the wafer was blown dry using high purity nitrogen.

The reactor is vertical cold-wall chamber with a rotating graphite susceptor (Φ = 2 in.). The source vapors were brought by flowing Ar carrier gas and then introduced into the reactor. High purity oxygen was used as reactive gas. The source and oxygen flux were both about 100 sccm. The work temperature of La/Hf mixing sources with 1:1 molar ratio was set to 200 °C. The reactor pressure was maintained at ~4.0 Torr during deposition processing using a dry pump to avoid the pollution of oil vapor. The substrate temperature ranged from 600 to 700 °C and deposition time from 3 to 45 min.

The post-annealing was performed at 750–900 °C for 3 min in N_2 by rapid thermal processing (RTP) to remove the residual impurity of the as-deposited films and further densify the oxide films.

Metal–insulator–semiconductor capacitors were fabricated by sputtering Pt top electrodes through a shadow mask with a diameter of 200 μm for electrical measurements.

The La content of La-doped HfO_2 films were determined by inductive coupled plasma (ICP). The interfacial structures and chemical bonding of the films were evaluated by X-ray photoelectron spectroscopy (XPS). The surface morphology was examined using atomic force microscopy (AFM). The film roughness was represented by the root mean square value (RMS) in 1 μm × 1 μm area. The physical thickness of high-*k* films was estimated by ellipsometer. The band gap was characterized by transparency spectroscopy using a UV–vis–NIR spectrophotometer. Capacitance–voltage (*C*–*V*) and leakage current density–voltage (*J*–*V*) characteristics were measured by Agilent 4294A precision impedance analyzer and HP4140B PA meter/dc voltage source, respectively.

3. Results and discussion

For ultrathin gate dielectrics oxide with several nanometers, the surface uniformity becomes more stringent for oxide reliability issues. Fig. 1 shows the AFM image of MOCVD-derived La-doped HfO_2 films deposited at 600 °C for 5 min. It has smaller surface roughness with RMS of ~0.5 nm.

ICP analyses reveal the La content in La-doped HfO_2 film deposited at 600 °C for 3 min was about 5 mol%. When the deposition time extends to 45 min, the La content in films reduces

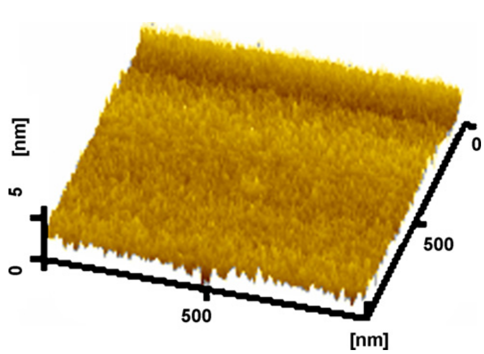

Fig. 1. AFM image of La-doped HfO_2 films on Si deposited at 600 °C for 5 min.

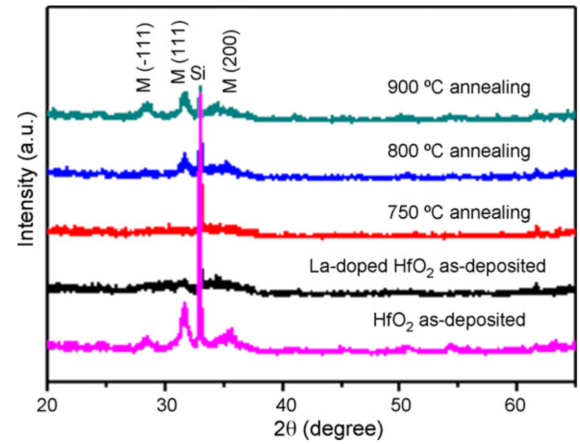

Fig. 2. XRD patterns of La-doped HfO_2 films on Si deposited at 600 °C for 45 min and annealed at various temperatures.

to 1%. This is due to the difference in evaporation pressure of $Hf(acac)_4$ and $La(acac)_3$ in the Hf/La mixing source. The sublimation temperatures of $Hf(acac)_4$ and $La(acac)_3$ are 195 and 240 °C (1 atm), respectively. Lower sublimation rate of $La(acac)_3$ results in the decrease of La element in the films with increasing growth time.

XRD was explored to characterize the structure of La-doped HfO_2 films. Fig. 2 shows the XRD patterns of 50 nm thick La-doped HfO_2 films deposited on Si at 600 °C for 45 min and annealed at various temperatures. Generally, HfO_2 and La_2O_3 films start to crystallize below 600 °C [3], while La-doped HfO_2 films show higher crystallization temperatures than pure La_2O_3 or HfO_2 [25]. In Fig. 2, the pure HfO_2 film has crystallized as-deposited and the La-doped HfO_2 films deposited at 600 °C show amorphous feature. And no crystalline peak is observed in 750 °C post-annealed La-doped HfO_2. However, after 800 °C post-annealing, the XRD patterns indicates that slight amount of HfO_2 monoclinic phase by the reflection at $2\theta = 31.6°$ appears in the films. The diffraction peaks from monoclinic phase become obvious after subsequent 900 °C post-annealing. Evidently, the incorporation of slight amount of La into HfO_2 has enhanced the crystallization temperature of the HfO_2 films to 750 °C.

In order to determine the intrinsic dielectric constant and remove the interface layer influence on Si substrates, La-doped HfO_2 films were deposited on $Pt/TiO_2/SiO_2/Si$ at 600 °C for 45 min. The metal–insulator–metal (MIM) capacitors were used to evaluate the dielectric constants of La-doped HfO_2 films. The thick film has a dielectric constant of ~28 at 1 MHz. The La-doped HfO_2 films with slight amount of La concentration show higher dielectric constant value than pure HfO_2 (~25). It is advantageous over other Hf-based amorphous materials such as $HfSiO_x$ and $HfAlO_x$.

XPS analyses were used to examine the composition and chemical bond of La-doped HfO_2 films on Si so as to further reveal the interfacial structure. The probe depth of XPS is only several nanometers. Based on the signal intensity and content of Si, we can deduce the interfacial status. The binding energies of core levels were calibrated by setting the adventitious carbon 1*s* peak at 284.6 eV.

Fig. 3(a) shows the XPS Si2*p* spectra of the films deposited at 600 °C for 3 min on Si. The two main peaks can be assigned to the Si–Si bond (~99.4 eV) and Si–O bond (~103.0 eV). This implies that some Si atoms have been linked to oxygen.

The XPS O1*s* spectra of the films on Si are shown in Fig. 3(b). The peak positions of O1*s* portion for La_2O_3, HfO_2, and SiO_2 are 528.5 eV, 530.7 eV [26], and 533.0 eV [23], respectively. The O1*s* peak position falls at 532.5 eV between HfO_2 and SiO_2. It indicates