Epitaxy Growth and Electrical Properties of La$_2$Hf$_2$O$_7$ Thin Film on Si(001) substrate by Pulsed Laser Deposition

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Abstract. La$_2$Hf$_2$O$_7$ (LHO) thin films have been epitaxially grown on Si(001) substrates using an ultrahigh vacuum pulsed laser deposition (PLD) system. The high-resolution transmission electron microscopy (HRTEM) results show the predominant orientation of LHO grown on Si(001) is (001)$_{\text{LHO}}$//(001)$_{\text{Si}}$ and [110]$_{\text{LHO}}$/[110]$_{\text{Si}}$, indicating a remarkable tendency of cube-on-cube epitaxy. The composition of the sample was investigated by X-ray photoelectric spectroscopy (XPS). High-frequency C-V characteristics for n-type MIS capacitors with epitaxial LHO film show that the dielectric constant (k value) of the LHO dielectrics is estimated approximately to be 22 from the accumulation area of 1M frequency C-V curves. I-V characteristic of the LHO dielectrics shows that the leakage current density is in an acceptable magnitude, ranging from $10^{-7}$ to $10^{-2}$ A/cm$^2$ in the voltage range from 0 to 3 V.

1. Introduction

The aggressive scaling of CMOS devices is driving SiO$_2$-based gate dielectrics to their physical limits [1-2]. Recently, complex rare earth (RE) and transition metal (TM) oxides (such as LaAlO$_3$, Dy$_{0.8}$Hf$_{0.2}$O$_x$, and La$_2$(Zr,Hf)$_2$O$_7$) attract considerable interests as candidate high-$\kappa$ gate dielectrics for silicon MOS devices [3-5]. La$_2$Hf$_2$O$_7$(LHO) is one of the promising high-$\kappa$ dielectrics for its significant advantages: (i) the crystallization temperature can be raised without lowering $\kappa$; (ii) La-based oxides have a larger conduction band offset and lower leakage current; (iii) LHO exhibits better adjustable work function ability with metal gate.

Epitaxial oxide thin films have been intensively investigated as high-$\kappa$ dielectrics because of their particular interfacial properties on Si substrates [6]. However, most of these oxides that have been epitaxially grown on Si(001) substrate are adopting the unfavorable orientation (such as (110)$_{\text{REZrO$_3$}}$//(001)$_{\text{Si}}$) which may cause twinning and other defects [7]. Therefore, to fabricate cube-on-cube epitaxy of metal oxides on Si(001) is a vital issue on high-$\kappa$ oxide preparation. Crystalline LHO is in pyrochlore phase with space group symmetry Fd$_3$m and has a little lattice mismatch of -0.74 % with respect to two times of Si(001) spacing at room temperature [8]. Therefore, it is quite suitable for epitaxial growth on Si substrate. Up until now, both molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) processes can be employed to grow the LHO films [9, 10]. In order to achieve further application, studies on the structural and electrical properties of the LHO film on Si(001) are significant.

In this paper, the epitaxial LHO films have been grown on Si(001) substrates using an ultrahigh vacuum PLD system. The interfacial composition and bonding states of the LHO/Si structure were
investigated by high-resolution transmission electron microscopy (HRTEM) and x-ray photoelectron spectroscopy (XPS). In addition, the epitaxial LHO thin films show promising electrical properties which are suitable for high-k dielectric application in the future.

2. **Experimental**

The LHO ceramic target with purity of 99.99% for PLD deposition was obtained by conventional sintering method. LHO thin films were grown by a ultra-high vacuum PLD system. Prior to the growth, the n-type Si(001) substrates with a resistivity of 2-5 Ω·cm were cleaned via a standard RCA cleaning process to obtain a H-terminated Si surface. The Si substrates were immediately transferred into the vacuum chamber. When the hydrogen atoms were completely removed from Si substrate surface at ~500 °C, a (2×1) reconstruction of reflection high-energy electron diffraction (RHEED) pattern indicated that a clean Si(100) surface was formed. The vacuum chamber was under 1 × 10⁻⁷ Torr during the deposition. Ultrathin LHO films were deposited using a KrF excimer laser running at 2 Hz repetition rate with an energy density of ~2 J/cm² focused at a growth rate of ~0.04 Å per pulse. The substrate temperature ranged from 700 to 850 °C during the film growth.

HRTEM was used to determine the crystallinity and structure of the LHO films. The chemical composition and bonding states of the films were investigated by XPS. The measurements were carried out in VG MK II spectrometer using monochromated Al Kα irradiation and Ar⁺ ions etching was performed for 5 mins. The electrical properties, such as capacitance-voltage (C-V) and current-voltage (I-V) characteristics, were measured by an HP 4284 LCR meter and a Keithley 2400 sourcemeter at room temperature respectively.

3. **Results and discussion**

HRTEM demonstrates the interface and crystallinity information of the epitaxial LHO films deposited at 780 °C. As shown in Fig. 1, LHO film and Si substrate reveals a good lattice matching and there is a slight interface in the HRTEM image. It is clearly observed that the LHO sample with uniform atomic pattern shows high crystallinity and has no distinguished grain boundary within all TEM observation. The orientation relationship between LHO and Si can be absolutely determined as [110]LHO//[110]Si and (001)LHO//(001)Si which is in agreement with the RHEED and Φ-scan results (not shown). The in-plane epitaxy of [001] LHO that is parallel with Si [001] suggests a super-cell lattice match, that is, the spacing of LHO [001] lattice (10.78 Å) matches that of twice of Si [001] (10.86 Å). The electron diffraction pattern of LHO layer in the inset further indicates a cubic structure in the LHO film.

![Figure 1. HRTEM image of the epitaxial LHO film on Si substrate.](image-url)
The chemical properties of the thin films were measured by XPS. Fig. 2 shows XPS Hf 4f, La 4d spectra for LHO thin films. The binding energies of the core level were calibrated by setting the adventitious C 1s peak at 284.6 eV. Fig. 2(a) is the Hf 4f spectrum of LHO film. Detailed curve fitting of the Hf 4f spectrum has been carried out with Shirley background and Gaussian-Lorentzian lines. In the fitting curves, there are two typical peaks at (i)~19 eV, (ii)~17.4 eV, corresponding 4f spin-orbit energy splitting which was calculated to be ~1.6 eV. It implies that Hf in the film presents in Hf 4+ state. Fig. 2(b) shows the XPS spectrum of La 3d portion of LHO. The binding energy and spin-orbit splitting energy of La 3d for LHO are similar to those for La2O3. According to the XPS data, the element composition has been calculated. The element ratio of La/Hf/O is 1.74:2:7.5 which is in agreement with the expected theoretical ratio. The XPS results indicate that the as-grown LHO film is in stable chemical state.

**Figure 2.** Core-level XPS spectra of (a) Hf 4f and (b) La 3d of epitaxial LHO thin film on Si substrate.

Fig. 3 shows high-frequency C-V characteristics for n-type MIS capacitors with 25 nm-thick epitaxial LHO film with Pt top electrodes. The circular Pt electrodes with diameter of 100 μm were sputtered through a shadow mask and the back contacts were made by evaporating Al. In the typical C-V traces, a transition from accumulation to depletion mode occurs at ~ 1.6 V. The capacitive effective thickness (CET) ~4.3 nm are extracted from the C-V curve without the quantum mechanical correction, and the dielectric constant (k value) of the LHO dielectrics is estimated approximately to
be 22 from the accumulation. The forward and backward measurements show a very small hysteresis below 0.1 V (~20 mV) indicating a very low density of defects causing hysteresis. The calculated flat-band voltage (VFB) is estimated to be ~0.6 V implying a negative flat band voltage shift, which can be attributed to positive charges arising from fixed charges or slow interface traps [11]. In addition, an obvious frequency dispersion phenomenon occurs in the accumulation area, indicating a larger interfacial state density.

**Figure 3.** C–V characteristic of a Pt/LHO/Si(001) MOS structure measured at high frequency.

I-V characteristic of the LHO dielectric is plotted in Fig. 4. The leakage current density is in an acceptable magnitude for the LHO film, ranging from 10–7 to 10–2 A/cm² in the voltage range from 0 to 3 V and the leakage current at 1 V is 10–4 A/cm². This result is relatively higher than that in other reports and need further investigation.

**Figure 4.** Current density J - voltage characteristic of a Pt/LHO/Si(001) MOS structure.

4. Conclusion

To conclude, we have epitaxially grown LHO film on Si(001) substrate using PLD method. The LHO film and Si substrate exhibit a cube-on-cube relationship [001]LHO//[001]Si and [110]LHO//[110]Si. The element composition of as-deposited LHO film is near stoichiometry. The capacitors show...
acceptable dielectric properties at room temperature; such as a dielectric constant of \( \sim 22 \), leakage current of \( 10^{-4} \) A/cm\(^2\) at 1 V for layers with 25 nm thickness.

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