Atomic layer-by-layer MOCVD of high-k dielectric thin films with in-situ monitoring by spectroscopic ellipsometry

Yoshishige Tsuchiya, Masato Endoh, Masatoshi Kurosawa, Raymond T. Tung, Takeo Hattori and Shunri Oda

Tokyo Institute of Technology, Research Center for Quantum Effect Electronics
2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan
Phone: +81-3-3734-3350 FAX: +81-3-3734-2542 E-mail: tsuchi@diana.pe.titech.ac.jp
'Musashi Institute of Technology, Department of Electrical and Electronic Engineering
1-28-1, Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

1. Introduction
The technological requirement to overcome the leakage current issue of ultra-thin gate SiO2 accelerates the research for alternative high-k materials [1]. Among several materials, Y2O3 is an alternative candidate because of a rather large band gap (~6eV), a high dielectric constant (ε~9-14), and a good chemical stability. Atomic layer-by-layer MOCVD is a key technique to deposit high-k thin films with good surface coverage and with large area uniformity[2]. In order to fabricate ultra-thin (~10nm) films with good reproducibility and good throughput, it is also important to establish a reliable technique to monitor the deposition process and to control it with atomic-layer precision. From these points of view, we have investigated the preparation of Y2O3 thin films by atomic layer-by-layer MOCVD combined with in-situ spectroscopic ellipsometry.

2. Experimental
The schematic diagram of the MOCVD growth chamber is shown in Fig. 1. O2 gas was used as the oxidization agent, Y(dpm)3 was used as the source for yttrium and was carried to the chamber by Ar gas. The concentration of Y(dpm)3 was maintained with a feedback controlled system using ultrasonic sensor EPISON II (Thomas Swan). In atomic layer-by-layer MOCVD, yttrium compound and oxygen were supplied alternatively. Major deposition parameters were the duration period of gas supply and the substrate temperature. Total pressure in the reaction chamber during deposition was 1.5 Torr. P-type Si (100) wafers on which 1nm nitride layer was prepared by direct nitridation at 800°C using NH3, were used as substrates to reduce the formation of SiO2 at the interface between Si and yttrium oxide. The substrate temperature (7s) was between 500 and 600 °C and SIMS analysis confirmed that no carbon impurities were incorporated in the oxide films. In-situ ellipsometry measurements were performed using a spectroscopic phase-modulated ellipsometer, UVISEL (Jobin-Yvon), which was installed to the reaction chamber.

3. Results and Discussion
Typical time evolution data of the real and imaginary parts of the pseudodielectric function spectra (ε(1)=ε1 + iε2), obtained by ellipsometry measurements during deposition of Y2O3, are shown in Fig. 2. A rapid change in the signals was observed during the initial deposition of up to about 5 nm. Differences from the initial values in ε1 and ε2 are related to the film thickness and these relationships have been used to evaluate the film thickness in-situ. In Fig. 3, trajectories of ellipsometry signals of two selected samples are plotted in the plane of ε1 and ε2 together with the corresponding surface morphology data for each sample. This result indicates a correlation between the trajectories on this plane and the surface morphology. Note that the RMS of the smoother sample is 0.26 nm, which is smaller than the thickness of a single layer of Y2O3, 0.30 nm. Cross-sectional TEM image of a 8 nm-thick Y2O3 film is shown in Fig. 4. In spite of the existence of the silicon nitride layer, an SiO2 layer was clearly observed. Therefore, a three-layer model is adequate to analyze the ellipsometry spectra at the initial stage of film growth. Electrical characteristics of an Au/Y2O3/Si/Al structure were plotted in Fig. 5. Leakage current densities of 100 A/cm2 and 10-7 A/cm2 at 1 V are obtained from the films with EOT's of 3.8 nm and 4.2 nm, respectively.

4. Conclusions
We demonstrated that spectroscopic ellipsometry is an effective method for in-situ monitoring of the fabrication of high-k dielectric thin films with the thickness of several nm by atomic layer-by-layer MOCVD. Thin Y2O3 films with a roughness smaller than the thickness of a single layer were obtained in the present study. Spectrum analysis of pseudodielectric function based on a three-layer model is expected to provide more information about the initial growth of ultra-thin films.

References

Fig. 1: A schematic diagram of the present MOCVD system.

Fig. 2: Real part ($\varepsilon_r$) and imaginary part ($\varepsilon_i$) of the pseudodielectric function spectra obtained by ellipsometry measurement during deposition of Y$_2$O$_3$ films. Substrate temperature $T_s = 500$ °C.

Fig. 3: Trajectories of ellipsometry signal in the plane of $\varepsilon_r$ and $\varepsilon_i$ from start to about 3nm-thick Y$_2$O$_3$ film deposition. AFM images of each film are also shown. $T_s = 560$ °C.

Fig. 4: Cross-sectional TEM image of a 8 nm-thick Y$_2$O$_3$ film. $T_s = 600$ °C.

Fig. 5: I-V and C-V characteristics of Y$_2$O$_3$ films with $T_s = 500$ °C and 600 °C.