HfO$_2$ films by UV assisted and thermal injection liquid source MOCVD.

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Introduction

High dielectric constant materials (‘high-k’) materials are receiving research attention as they introduce the possibility of scaling CMOS technology to 10-30 nm feature sizes [1]. HfO$_2$ has been studied widely due to its high dielectric constant (16-18 for monoclinic HfO$_2$) and due to its reasonable compatibility with polysilicon gate technology [2]. In this work we present the physical and electrical properties of HfO$_2$ films (2.4 nm to >100nm) formed on Si(100) by UV assisted (222nm) assisted and thermal injection liquid source MOCVD.

Experiments

The starting substrates were 2-4 Ωcm (100) orientation silicon, which received standard SCI/SC2 cleans. A range of surface preparation were explored, including: UV N$_2$O on the chemical oxide, RTN of the chemical oxide in NH$_3$ at 670°C, and HF last. The HfO$_2$ layers were deposited from a Hf(C$_3$H$_7$O)$_2$[OC(CH$_3$)$_2$CH$_2$OCH$_3$]$_2$ precursor in octane from 350 to 450°C using a liquid injection MOCVD, and also with a UV assisted (KrCl$^*$ 222nm) liquid injection MOCVD [3]. Film thicknesses from 2.5 nm to > 100 nm were deposited. Physical analysis was by TEM, X-ray reflectrometry and atomic force microscopy. Electrical analysis performed on thermally evaporated gold or mercury gate contact MIS structures.

Results

Physical analysis by TEM indicated that for 350 to 450°C the HfO$_2$ films exhibit a mixed amorphous/crystalline phase, the nanocrystals exhibiting the monoclinic structure. Figures 1 and 2 show HRTEM for films by thermal and UV assisted MOCVD respectively. The figures illustrate that the techniques can form continuous HfO$_2$ films to 2.4 nm. The interface oxide layer has been observed to decrease with the thickness of the HfO$_2$ film. The growth rate of the HfO$_2$ is 0.04 to 0.1 nm/injection for the UV and thermal liquid injection MOCVD processes. X-ray reflectrometry for the sample in Figure 1 indicated 2.2nm with a surface roughness of 0.6 nm, in good agreement with the HRTEM. The density of the films from X-ray reflectrometry is 8.9 to 9.0 g/cm$^3$, which is below the reported HfO$_2$ value of 9.68 g/cm$^3$. A further relevant observation from the TEM analysis is that the HfO$_2$ films are continuous on a HF last surface, which is not generally the case for HfO$_2$ by atomic layer epitaxy [4].

Electrical measurements on relatively thick (10-100 nm) films, where the effect of the interface oxide can be neglected, yield HfO$_2$ relative permittivity values in the range 15-19, in agreement with theoretical calculations for the monoclinic phase [5]. An example HFCV (1kHz to 100 kHz) is shown in Figure 3 for a 350°C deposited HfO$_2$ film (3.4 nm by HRTEM). For the low temperature deposited films interface defects are detected, consistent with un-passivated P$_{b0}$(P$_{b1}$) centers [6]. An equivalent oxide thickness value of 2.4 nm (not corrected for silicon differential capacitance or quantum mechanical effects) has been achieved, with leakage current densities of 10$^{-8}$ to 10$^{-7}$ A/cm$^2$ at 1 volt.

References


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Figure 1. HRTEM image of a 2.6 nm HfO$_2$ layer formed by liquid injection MOCVD at 450°C following a HF / NH$_3$ 670°C surface preparation. The interface oxide layer is 0.75 nm.

Figure 2. HRTEM image of a 2.4 nm HfO$_2$ layer formed by UV assisted liquid injection MOCVD at 400°C following a SCI/SC2 surface preparation. The interface oxide layer is 1.25 nm.

Figure 3. Example HFCV and JV (inset) for a HfO$_2$ film by thermal injection liquid source CVD. T$_{de} = 3.2$ nm (uncorrected) and J @-1 V ~ 10$^{-8}$ A/cm$^2$. (No forming gas anneal performed).