HfO_2 films by UV assisted and thermal injection liquid source MOCVD.

PK Hurley[1], BJ O'Sullivan[1], M.Modreanu [1], F.Roussel [2] ,
H Roussel[2], MA Audier[2], C.Jimenez, JP Senateur[2],
H.Davies[3], S.Rushworth[3], IW Boyd[4], Q.Fang[4],
H.Guillon[5]. (phurley@nmrc.ie)

[1] NMRC, Cork, Ireland
[2] INPG, Grenoble, France
[3] EPICHEM, Bromborough, UK
[4] University College London, UK
[5] JIPELEC, Meylan, France

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 SC1/SC2 cleans. A range of surface preparation were explored, including: UV N_2O 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 $Hf(C_3H_9O)_2(OC(CH_3)_2CH_2OCH_3)_2$ 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 crystallites 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-passiavated $P_{b0}/(P_{b1})$ 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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Acknowledgement

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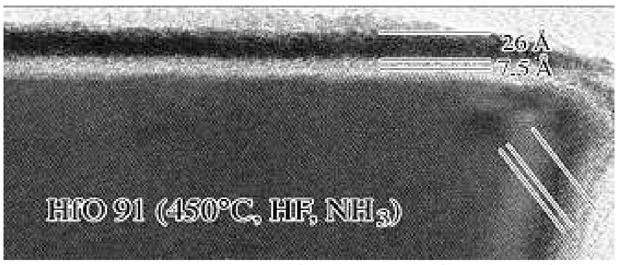

Figure 1. HRTEM image of a 2.6 nm HfO_2 layer formed by liquid injection MOCVD at 450°C following a HF / NH_3 670°C surface preparation. The interface oxide layer is 0.75 nm.

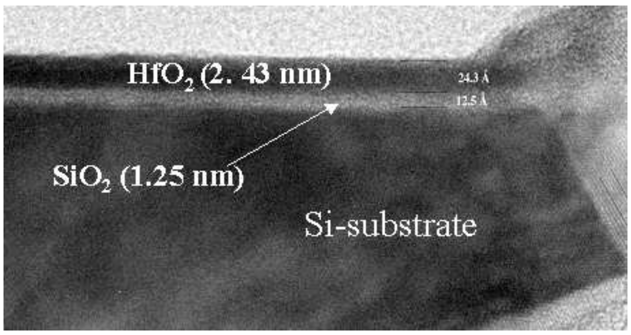

Figure 2. HRTEM image of a 2.4 nm HfO_2 layer formed by UV assisted liquid injection MOCVD at 400°C following a SC1/SC2 surface preparation. The interface oxide layer is 1.25 nm. (No UV N_2O for this sample)

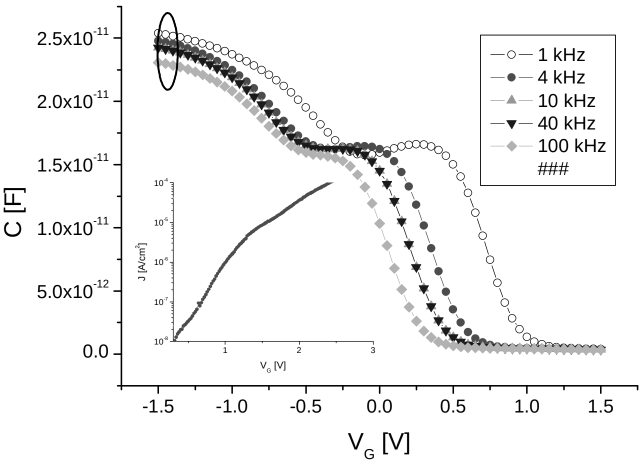

Figure 3. Example HFCV and JV (inset) for a HfO_2 film by thermal injection liquid source CVD. T_{eq} = 3.2 nm (un-corrected) and J @-1 V ~ 10^{-6} A/cm^2. (No forming gas anneal performed).