HfO_2 FILMS OBTAINED BY INJECTION MOCVD

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Abstract

Hafnium oxide (HfO_2) has received intensive attentions as it is an attractive material for alternative gate dielectrics due to its high dielectric constant (k~25) (1) and thermal stability in contact with silicon.

HfO_2 films were deposited at low temperature (275–550°C) by injection metalorganic chemical vapor deposition (I-MOCVD). A solution of Hafnium tetra-t-butoxide [$Hf(OtBu)_4$] in hexane (15% v/v) was used as precursor. No influence of the deposition atmosphere (reducing, oxidizing, or neutral) on the deposition yield was found (Fig 1). The deposition rate is mainly temperature dependent for this deposition temperature range.

The films were characterized by XRD, TEM, and FTIR. A post-deposition treatment at 800°C in oxygen or argon was also performed.

The samples can be divided in two groups: low temperature samples (T≤350°C) and high temperature samples (T> 350°C). There are several differences between these groups: films deposited at low temperature are mainly amorphous, and less dense, leading to a lower refractive value. For high temperature samples, the XRD diagrams and FTIR spectra show an increasing crystallinity that correlates with a monoclinic phase. The refractive index for these samples stabilizes around 2. TEM observations have allowed to establish that even at very low temperature, the films have a percentage of crystalline state.

The effect of the thermal treatments is different for the two groups of samples, and it depends on the annealing atmosphere. The interface HfO_2/Si is very sensible to the annealing. TEM cross view has allowed to determine the presence of a native SiO_2 films. The thickness of this layer increases when annealed in oxygen, mainly in the low temperature samples

Permittivity values (15-19) are also in agreement with the monoclinic phase[1]. The porous character of the films do not seem affect the JE characteristics; in fact, the leakage current densities are lower and the breakdown fields are higher in all cases for the amorphous samples than crystalline samples. For both type of samples, and the oxygen annealing presents a more pronounced effect than the argon annealing (Fig. 2). For the oxygen treated samples, the leakage current value was < 10^{-8}A/cm^2 at 1MV/cm.

Acknowledgements

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References

1 X. Zhao, D. Vanderbilt. Phys. Rev. B. 65, (2002) 233106.

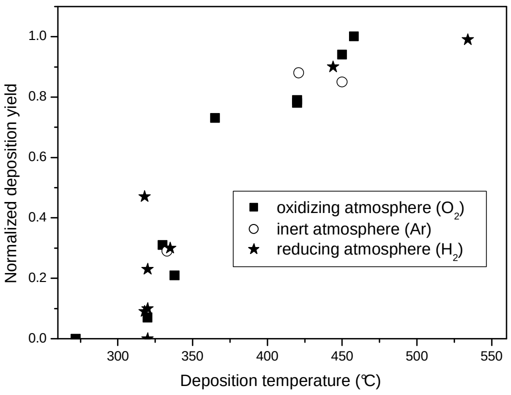

Figure 1. Evolution of the deposition yield (thickness/injected mol of precursor) with temperature, for oxidizing, reducing and neutral atmosphere.

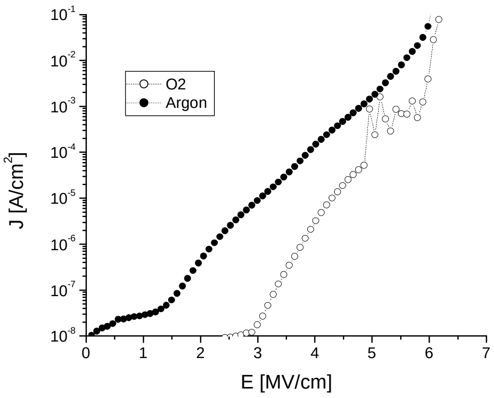

Figure 2. JE curves for the sample deposited at low temperature and treated under O2 and Ar.