Modeling of HfO₂ Film Deposition from Hf(MMP)₄

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Introduction

High-k gate dielectrics are necessary for sub-100-nm MOS transistors. Of the many possible high-k materials, metal oxide (such as HfO₂, ZrO₂, Al₂O₃, Ta₂O₅) shows promise as its k value is several times that of SiO₂. To develop the processes and apparatus for manufacturing high-k gate dielectrics, the chemical reaction mechanism should be properly understood. For this purpose, we modeled HfO₂ film formation using molecular orbital calculations and experimental analysis.

Experiment

A cold-wall-type MOCVD reactor was used to make the HfO₂ film. A wafer was heated with a heater and placed below the shower head plate. The liquid source, Tetrakis(1-Methoxy-2-methyl-2-roppoxy)Hafnium (Hf(MMP)₄), passed through the liquid mass flow controller, vaporizer and shower head plate and formed the HfO₂ film on the wafer.

Computations

The molecular orbital calculations were done using a GAMESS¹ program package at the B3LYP theory level. The basis sets were 3-21G for carbon, hydrogen and oxygen and LANL2DZ for hafnium. The binding energies of Hf(MMP)₄ were more than 300 kJ/mol. The enthalpy change ΔH for the reaction generating alcohol, which is the ΔH for the reaction of Hf(MMP)₄ with H₂O, was ~32 kJ/mol. The ΔH for β-elimination of Hf(MMP)₄ was 117 kJ/mol. Based on these calculations, we proposed a reaction model for the formation of HfO₂ film as follows. First, the reaction generating alcohol occurs between the OH terminated at the HfO₂ film surface and the Hf of the Hf(MMP)₄ molecules (Fig. 1 (a)). Then, the HfMMP is adsorbed on the surface (Fig. 1 (b)). Next, β-elimination occurs and a part of the MMP is desorbed. Then, the OH terminated surface is formed (Fig. 1 (c)). These reactions occur repeatedly, forming the HfO₂ film.

The rate constants for these reactions were estimated from the experimental data. The value for k₁, which is the reaction rate constant for the reaction generating alcohol, is 4.9x10⁻¹⁸ and that for k₂, which is the reaction rate constant for β-elimination, is 8.6x10⁹ exp(-17000/T). The deposition rate was able to be predicted by using these reaction rate constants.

Conclusion

We proposed a model for HfO₂ film deposition from Hf(MMP)₄. Reactions generating alcohol and β-elimination occur repeatedly to form HfO₂ film. We determined the reaction rate constants (k₁, k₂) by fitting the calculated results against the experimental data. We proved that our model could be used to predict the deposition rate of HfO₂ film.

Reference


Fig. 1 Reaction model for HfO₂ film deposition using Hf(MMP)₄