Modeling of HfO_2 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 HfO_2, ZrO_2, Al_2O_3, Ta_2O_5) shows promise as its k value is several times that of SiO_2. 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 HfO_2 film formation using molecular orbital calculations and experimental analysis.

Experiment

A cold-wall-type MOCVD reactor was used to make the HfO_2 film. A wafer was heated with a heater and placed below the shower head plate. The liquid source, Tetrakis(1-Methoxy-2-methyl-2roppoxy)Hafnium ($Hf(MMP)_4$), passed through the liquid mass flow controller, vaporizer and shower head plate and formed the HfO_2 film on the wafer.

Computations

The molecular orbital calculations were done using a GAMESS[1] 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 H_2O, 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 HfO_2 film as follows. First, the reaction generating alcohol occurs between the OH terminated at the HfO_2 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 HfO_2 film.

The rate constants for these reactions were estimated from the experimental data. The value for k_1, which is the reaction rate constant for the reaction generating alcohol, is 4.9×10^{-21} and that for k_2, which is the reaction rate constant for β-elimination, is 8.6×10^{9} exp(-17000/T). The deposition rate was able to be predicted by using these reaction rate constants.

Conclusion

We proposed a model for HfO_2 film deposition from $Hf(MMP)_4$. Reactions generating alcohol and β-elimination occur repeatedly to form HfO_2 film. We determined the reaction rate constants (k_1, k_2) by fitting the calculated results against the experimental data. We proved that our model could be used to predict the deposition rate of HfO_2 film.

Reference

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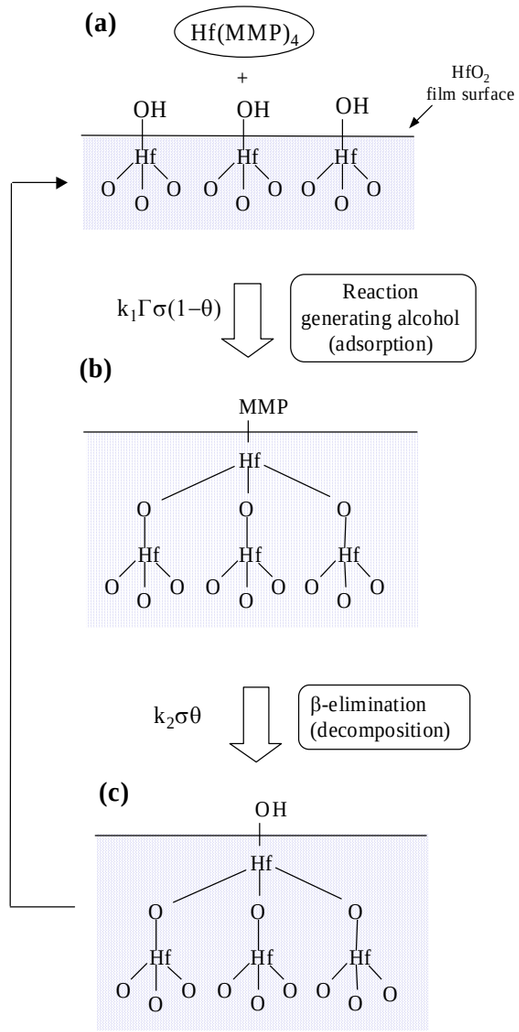

k_1, k_2 : reaction rate constant

Γ : incident flux of $Hf(MMP)_4$

θ : $\dfrac{\text{number of MMP}}{\text{number of (MMP+OH)}}$

Fig. 1 Reaction model for HfO_2 film deposition using $Hf(MMP)_4$