Developing routes toward atomic layer deposition of tungsten using fluorine-free W precursor and various reactants with density functional theory

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The W-ALD process using WF_6 is applied to the fabrication of the nucleation layer for W-plug and W gate or bit line in the current semiconductor device manufacturing. However, the highly corrosive nature of the F contained in the precursor, damages the underlying oxide and metal film, and degrade the electrical characteristics and reliability of the device. Therefore, it is necessary to develop an ALD process with F-free W (FFW) precursor. In this study, $EtCpW(CO)_3H$ is selected as a FFW metal-organic precursor, while suitable reactants (reducing agents) among various ones, molecular H_2, H_2 plasma (which provides highly reactive H radical), trimethyl aluminum triethyl aluminum, TBH (tert-butyl hydrazine), diethylamineborane (DEAB), dimethylamineborane (DMAB) NH_3 etc. are adopted based on the density functional theory (DFT) calculation. Following the DFT predictions, successful ALD-W films are prepared using the reducing agents diethylamineborane (DEAB) and H_2 plasma at a deposition temperature of 325°C. The growth rate observed using DEAB reactant is ~1.3Å /cycle. On the other hand, H_2 plasma, as a reactant, offers relatively lower growth rate of ~ 0.4 Å/cycle. The crystalline and amorphous phase of the as-deposited W films are confirmed using X-ray diffraction (XRD) for H_2 plasma and DEAB, respectively, Furthermore, the XRD reveals a mix-phase of β-W and tungsten carbide (WC) for the films grown by H_2 plasma and the X-ray photoelectron spectroscopy analyses confirm considerable impurities (Boron, Carbon, Nitrogen, Oxygen) in the films grown by DEAB. However, a post-annealing could further improve the properties of these films.

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