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Characteristic of Ru Thin Film Deposited by ALD

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Recently, many platinoid metals like platinum and ruthenium have been used as an electrode of microelectronic devices because of their low resistivity and high work-function. However the material cost of Ru is very expensive and it usually takes long initial nucleation time on SiO2 during chemical deposition. Therefore many researchers have focused on how to enhance the initial growth rate on SiO2 surface. There are two methods to deposit Ru film with atomic layer deposition (ALD); the one is thermal ALD using dilute oxygen gas as a reactant, and the other is plasma enhanced ALD (PEALD) using NH3 plasma as a reactant. Generally, the film roughness of Ru film deposited by PEALD is smoother than that deposited by thermal ALD. However, the plasma is not favorable in the application of high aspect ratio structure. In this study, we used a bis(ethylcyclopentadienyl)ruthenium [Ru(EtCp)2] as a metal organic precursor for both thermal and plasma enhanced ALDs. In order to reduce initial nucleation time, we use several methods such as Ar plasma pre-treatment for PEALD and usage of sacrificial RuO2 under layer for thermal ALD. In case of PEALD, some of surface hydroxyls were removed from SiO2 substrate during the Ar plasma treatment. And relatively high surface nitrogen concentration after first NH3 plasma exposure step in ALD process was observed with in-situ Auger electron spectroscopy (AES). This means that surface amine filled the hydroxyl removed sites by the NH3 plasma. Surface amine played a role as a reduction site but not a nucleation site. Therefore, the precursor reduction was enhanced but the adhesion property was degraded. In case of thermal ALD, a Ru film was deposited from Ru precursors on the surface of RuO2 and the RuO2 film was reduced from RuO2/SiO2 interface to Ru during the deposition. The reduction process was controlled by oxygen partial pressure in ambient. Under high oxygen partial pressure, RuO2 was deposited on RuO2/SiO2, and under medium oxygen partial pressure, RuO2 was partially reduced and oxygen concentration in RuO2 film was decreased. Under low oxygen partial pressure, finally RuO2 was disappeared and about 3% of oxygen was remained. Usually rough surface was observed with longer initial nucleation time. However, the Ru deposited with reduction of RuO2 exhibits smooth surface and was deposited quickly because the sacrificial RuO2 has no initial nucleation time on SiO2 and played a role as a buffer layer between Ru and SiO2.

Keywords: Ruthenium, atomic layer deposition, initial nucleation time