Formation of Highly Pure Nickel Films by Hot-wire-assisted ALD

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Abstract
We successfully formed highly pure Ni films by atomic layer deposition (ALD) coupled with hot-wire-assistance (HW) system at low substrate temperature of 250°C using nickelocene (NiCp₂) and NH₃ as a precursor and reductant, respectively. Thanks to efficient decomposition of NH₃ by HW system, carbon content could be decreased to 1% and nitrogen was under detection limit of XPS.

1. Introduction
Nickel and its silicide are promising materials for contact electrode and metal gates of MOSFETs. In recent years, it was introduced for the metal electrode in metal-insulator-metal (MIM) capacitor such as unipolar resistive random access memory (unipolar ReRAM) due to its high work function (5.15 eV) and compatibility with CMP process. Atomic layer deposition (ALD) is a most strong candidate for future-generation technology due to its excellent step coverage, atomic scale thickness controllability, and film uniformity.

Ni deposition by conventional thermal ALD, however, cannot prevent the residual contamination in the film (C, O, and N), and plasma-ALD induces the damage to underlying materials. Here, we propose a novel method of hot-wire-assisted ALD (HW-ALD) overcoming the issues possessed by above-mentioned conventional ALD processes.

Based on our quantum chemical calculations, we found that NH₂ radical is more reactive than other radicals such as H radical, and hot-wire assisted cracking of NH₃ may be the best way to supply NH₂ radical.

2. Experimental
An in-house ALD system installing tungsten hot wire (1cm above the substrate) was employed, which promotes decomposition reaction of NH₃ into NH₂ radical. The base pressure was about 1×10⁻⁵ Pa. To avoid oxygen contamination, oxygen-free precursor (NiCp₂) was selected, which was supplied to the reactor via bubbler using He carrier gas. Procedure adopted in this study was as follows: (1) supplying the precursor to adsorb on the substrate, (2) purging the remaining precursor by He, (3) supplying NH₃ and simultaneously turning on the tungsten filament (HW became 1350°C), (4) turning off the filament, and purging the remaining reductant and by-products by He.

The deposition temperatures were changed from 250°C to 350°C.

3. Results and Discussion
Growth per cycle (GPC) was increased with increase of NH₃ feeding time, and saturated at long feeding time (Fig.1). Underlying materials did not influence the GPC largely (0.61 Å on SiO₂, 0.69 Å on Si). This may be caused by different incubation time on different underlayers. Meanwhile, carbon content decreased with increase of NH₃ feeding time and became almost constant for different temperature of 250°C and 350°C (Fig.2). The lowest carbon content achieved in this study was about 1% at 250°C, and the Ni film resistivity at this condition was 27 μΩ-cm without a post-anneal. Nitrogen contamination was not detected by XPS despite using NH₃.