

## Formation of Highly Pure Metallic Ruthenium Film Using Hot-wire-assisted Atomic Layer Deposition for Electrode Applications

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**Abstract:** We successfully formed highly pure Ru films by atomic layer deposition (ALD) coupled with hot-wire-assistance (HW) system using ruthenocene ( $\text{RuCp}_2$ ) and  $\text{NH}_2$  radicals under non-oxidative ambient.  $\text{NH}_2$  radicals were produced by cracking  $\text{NH}_3$  with the aid of HW. Purity of the resulting Ru film was confirmed by X-ray photoelectron spectroscopy (XPS) and C-V measurement.

**1. Introduction:** Ru thin films have been extensively studied for various applications including a capacitor electrode of dynamic random access memories (DRAMs). It requires a uniform film thickness within the deep trenches, and thus ALD is a preferred solution. However, Ru deposition by conventional thermal ALD cannot prevent oxidation of underlayer during deposition due to usage of oxygen. It therefore leads to insufficient thermal stability of the effective work function (EWF). Although plasma-enhanced (PE-ALD) is another candidate, it induces the plasma damage to the underlayer. Recently, we have proposed a novel ALD process coupling with hot-wire-assistance, called HW-ALD. It overcomes the above-mentioned issues. Depositions of highly pure Co and Ni films using HW-ALD have already been demonstrated [1, 2], and Ru deposition was studied in this report.

**2. Experimental:** An in-house ALD system installing tungsten hot wire was employed, which promotes decomposition reaction of  $\text{NH}_3$  into  $\text{NH}_2$  radical. Details of the process can be found in our previous reports [1,2]. To avoid oxygen contamination, oxygen-free precursor ( $\text{RuCp}_2$ ) was selected, which was supplied to the reactor via bubbler using He carrier gas. Cyclic procedure was adopted: (1) supplying the precursor to adsorb on the substrate, (2) purging the remaining precursor by He, (3) supplying  $\text{NH}_3$  and simultaneously turning on the tungsten filament, (4) turning off the filament, and purging the remaining reductant and by-products by He. The deposition temperature was set at  $300^\circ\text{C}$ . Composition of the film was characterized by XPS. EWF was evaluated by C-V measurement by fabricating pMOS on n-type silicon substrate ( $8.9 \times 10^{15} \text{ cm}^{-3}$ ) and Ru electrode (20 nm). PVD-Au film was used as reference.

**3. Results and Discussion:** Obtained Ru film was highly pure without incorporation of oxygen and nitrogen impurities (Fig.1). After analyzing the XPS intensity ratio of Ru  $3d_{3/2}$  to  $3d_{5/2}$ , we found its area ratio was near  $2/3$  (not shown here), which indicates carbon impurity seemed also low. Then, EWF of the Ru film was measured (Fig.2), and it was estimated as  $4.83 \pm 0.05 \text{ eV}$ . Considering that EWF of PVD-Ru and thermal ALD-Ru films were reported as  $4.85 \text{ eV}$  and  $5.1 \text{ eV}$ , minor difference of EWF between PVD-Ru and our Ru films confirmed free from oxygen in HW-ALD Ru film at  $300^\circ\text{C}$ .

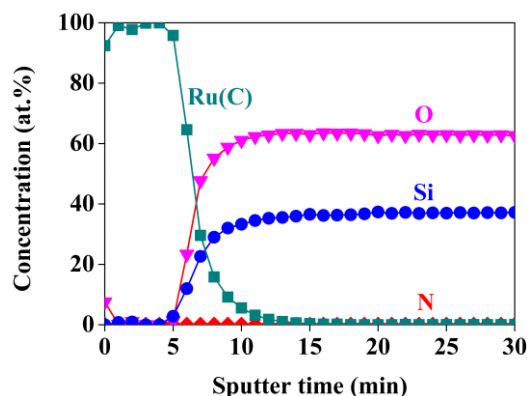


Fig. 1 X-ray photoelectron spectroscopy (XPS) depth profile of Ru film on  $\text{SiO}_2$  at  $300^\circ\text{C}$

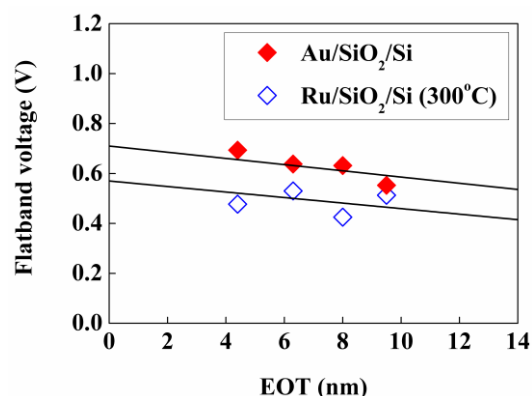


Fig. 2 Flatband voltage versus oxide thickness for Ru film formed at  $300^\circ\text{C}$ , compare with PVD Au.

[1] H. Shimizu, et al. JVST. A **30**, 01A144 (2012).

[2] G. Yuan, et al. JVST. A, **32**, 01A104 (2014).

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