

## A-7-1 (Invited)

## Atomic Layer Deposition of PMOS Metal Gate Electrodes and High-k/Metal Interface Reactions for Advanced Device Applications

G.N. Parsons, K.J. Park, D.B. Terry

Department of Chemical and Biomolecular Engineering  
North Carolina State University, Raleigh, NC 27695

## 1, Introduction:

Improved control of interface reactions during thin film processing is critical for advanced electronic devices<sup>1</sup>. Atomic layer deposition (ALD) can be used to achieve well controlled reaction chemistry during film deposition to achieve desired interface structure. Ruthenium is of interest for advanced metal/oxide/semiconductor (MOS) transistor gate electrodes to reduce poly-silicon depletion effects and as nucleation layer for copper interconnect layers.<sup>2</sup> We have studied ALD of Ru as a PMOS gate metal candidate, including studied interface reactions during thermal and plasma deposition of Ru and RuO<sub>x</sub> films from various precursors. Recent work has also extended to other PMOS metal candidates including rhodium and rhenium.

## 2. Results and Discussion:

*ALD ruthenium and rhodium*

ALD Ru was carried out in a home-built hot-wall quartz tube reactor using RuCp<sub>2</sub> (bis-(cyclopentadienyl)ruthenium) as a precursor and dry oxygen. Rhodium ALD was carried out using Rh(acac)<sub>3</sub> and dry air. For ALD processing, the precursor and oxidant gas was introduced into the reactor in separate pulses (typically 3 and 6 sec, respectively) with a 20 second Ar purge between each reactant. Argon was also used as a carrier gas for the metal precursor pulse. Under these conditions, self limiting growth was observed corresponding to ~1 Å per deposition cycle. Capacitance vs. voltage (CV) was measured using an HP 4284A LCR meter at 1MHz using p-type silicon substrates with doping levels of  $1.5 \times 10^{18} \text{ cm}^{-3}$ .

Figure 1 shows Ru film thickness vs. number of ALD cycles for deposition on HfO<sub>2</sub>/SiO<sub>2</sub>, SiO<sub>2</sub> and hydrogen-terminated silicon (HF-last) surfaces. For deposition on the Si-H surface, no film was observed by eye after 100 cycles for the conditions used. We have also studied selective area ALD of Ru metal for gate electrode applications using contact printed self assembled monolayer resists<sup>3</sup> to enable direct formation of Ru/HfO<sub>2</sub>(SiO<sub>2</sub>)/Si capacitor stacks. The inset in Figure 1 is an optical image of a selectively deposited Ru capacitor on HfO<sub>2</sub>. The deposited thickness per cycle was similar on SiO<sub>2</sub>, HfO<sub>2</sub>/SiO<sub>2</sub>, and Si-H, but the intercepts show different values,

consistent with different nucleation processes for growth on these surfaces. We have recently initiated work on ALD rhodium and rhenium, and growth per cycle as a function of temperature of Rh is similar to results for Ru from Ru(Cp)<sub>2</sub>.

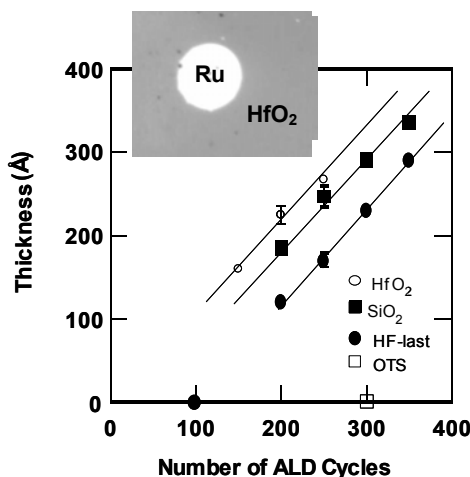


Figure 1. Ru thickness vs. number of ALD cycles various substrates. The inset shows a selectively deposited Ru dot on HfO<sub>2</sub>.

*Characterization of effective work function*

A key question for advanced gate metals is the work function of the metal in the capacitor structure.<sup>4</sup> For the case of negligible bulk dielectric charge,  $V_{FB}$  plotted versus EOT for a series of capacitors with different dielectric thicknesses will be linear, and  $\Phi_{ms}$  can be obtained from the intercept. For the case of internal dielectric interfaces, a single plot of  $V_{FB}$  vs EOT is not sufficient to unambiguously differentiate the different interface charge densities, but a reasonable estimate of  $\Phi_{m,eff}$  (and changes in  $\Phi_{m,eff}$ ) can be made.

For Ru on SiO<sub>2</sub> and SiO<sub>2</sub>/HfO<sub>2</sub>, CV curves were analyzed for a range of dielectric film thickness, and the results of  $V_{FB}$  versus EOT are shown in Figure 2. In this case,  $\Phi_{m,eff}$  is determined to be  $4.84 \pm 0.05 \text{ eV}$  on SiO<sub>2</sub> and  $4.70 \pm 0.1 \text{ eV}$  SiO<sub>2</sub>/HfO<sub>2</sub>. For the ALD Ru films deposited from Ru(Cp)<sub>2</sub>, Auger analysis indicates O/Ru ratio of ~3% and resistivity values ranged from 35 to  $20 \mu\Omega \cdot \text{cm}$ .

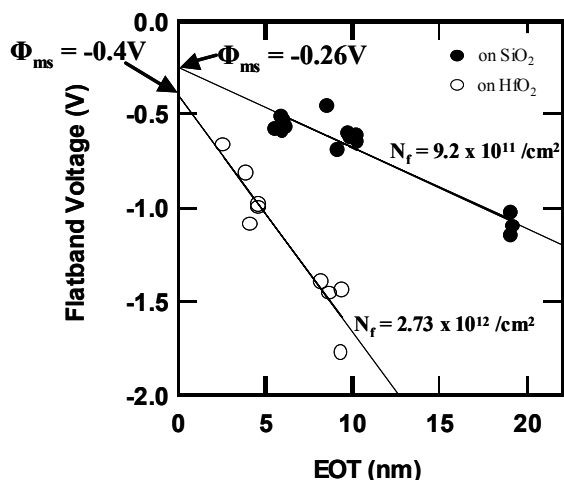


Figure 2.  $V_{FB}$  versus EOT for Ru/SiO<sub>2</sub>/Si and Ru/HfO<sub>2</sub>/Si Capacitors. The intercept gives  $\Phi_{m,eff} = 4.84\text{eV}$  on SiO<sub>2</sub> and  $4.7\text{eV}$  on HfO<sub>2</sub> surfaces

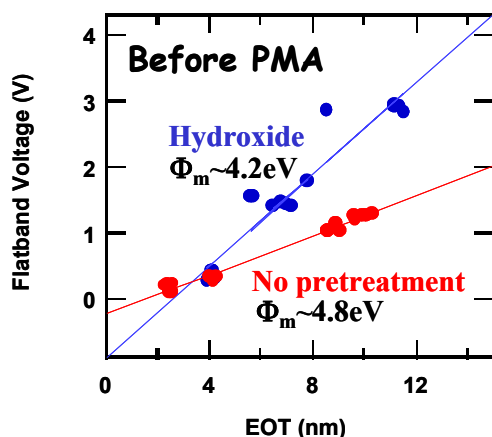


Figure 3.  $V_{FB}$  versus EOT for Ru where the starting substrate was treated with HNO<sub>3</sub> to form surface hydroxyl groups.

Methods to modify and tune the effective metal workfunction are also of interest. Shift can be caused by intrinsic charge transfer at the metal/dielectric interface, or extrinsic effects, including dipoles resulting from interface chemical bonds. We have explored various surface treatments before metal ALD to modify the effective metal workfunction, and Figure 3 shows that large changes are possible with chemical treatments. However, these treatments are generally not stable to post metal anneals.

We have deposited plasma RuO<sub>2</sub> metal from (Ru[tmhd]) introduced downstream from a remote plasma containing either N<sub>2</sub>O or H<sub>2</sub>, and examined the interface structure using Auger and X-ray photoelectron spectroscopies. Figure 4 shows XPS results for thin ( $\sim 75\text{\AA}$ ) RuO<sub>2</sub> films deposited on HfO<sub>2</sub> using H<sub>2</sub> or N<sub>2</sub>O plasma at 500°C. The film

deposited with N<sub>2</sub>O plasma shows a shift to higher binding energy, consistent with Hf-O-Ru bonding at the interface, where the higher electronegativity of Ru (relative to Hf) increases the binding energy of the Hf 4f electrons. For the case of RuO<sub>x</sub> films deposited from H<sub>2</sub> plasma, a decrease in the Hf 4f binding energy is observed, consistent with reduction of the HfO<sub>2</sub>, possibly forming some Hf-Ru bonds.

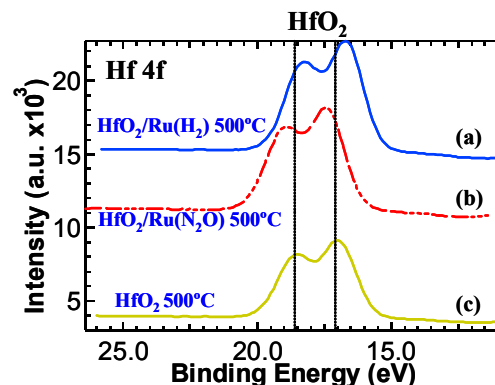


Figure 4. Hf4f spectra of HfO<sub>2</sub> and thin RuO<sub>x</sub> films on HfO<sub>2</sub> dielectric.

#### *Spectroscopic Studies of Interface Processes in ALD Metal Gates*

We have begun to study initial phases of ALD metal growth using XPS, AES and in-situ IR to better understand the role of surface preparation on metal film nucleation, the composition of metal films at the metal/dielectric interface, and possible reaction processes and interface layers at metal/high-k interfaces. In-situ infrared spectroscopy has been used to examine initial phases of ALD film growth for metal deposition on oxide surfaces, and also for high-k (HfO<sub>2</sub>) deposition on hydrogen terminated Si. Quantitative analysis of the reflectivity signals, and comparison of reflectivity with data from other analyses, are expected to give more insight into specific mechanisms for ALD of metal growth on oxides.

We acknowledge support from SEMATECH and the Semiconductor Research Corporation, and support from NSF.

#### **References**

- <sup>1</sup> V. Misra, G. Lucovsky, and G. N. Parsons, MRS Bulletin March (2002).
- <sup>2</sup> H. Kim, Journal of Vacuum Science and Technology B **21**, 2231 (2003).
- <sup>3</sup> K. J. Park, J. M. Doub, T. Gougousi, et al., Applied Physics Letters **86**, 051903 (2005).
- <sup>4</sup> R. Jha, J. Gurganos, Y. H. Kim, et al., Ieee Electron Device Letters **25**, 420 (2004).