



## *In-situ* analysis on the initial growth of ultra-thin ruthenium films with atomic layer deposition

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### ABSTRACT

The initial growth behavior of ruthenium during the thermal-activated atomic layer deposition (ALD) using [(ethylcyclopentadienyl)(pyrrolyl)ruthenium(II)] (ECPR) and molecular oxygen was investigated in a cluster tool combining an ALD reactor with a surface analysis unit under high vacuum conditions. A direct qualification and quantification of the chemical surface composition by X-ray photoelectron spectroscopy (XPS) and a determination of the surface topography by atomic force microscopy (AFM) were conducted in the course of the ALD cycles without vacuum break. XPS revealed a substrate-inhibited Ru growth on a hydrogen-terminated silicon surface, which was preceded by an incubation period of 20 ALD cycles. The Si surface oxidized during the first 50 cycles. AFM measurements showed a roughness maximum around the 40th ALD cycle, which suggested an island growth mode and thus corresponded with the substrate inhibition. As verified from the AFM data with an analytical model by Nilsen et al. the Ru islands coalesced between the 40th and 50th ALD cycle. The ALD growth initiation of Ru was also investigated on aluminum oxide and tantalum nitride. XPS revealed a similarly inhibited growth behavior on all the investigated substrates. However, the ECPR adsorption during the very first Ru precursor pulse differed as the amount of chemisorbed Ru on the  $\text{NH}_2$ -terminated  $\text{TaN}_x(\text{O}, \text{C})$  surface was much higher compared to the OH-terminated  $\text{Al}_2\text{O}_3$  and the H-terminated Si surface. Summarizing, we demonstrated that *in-vacuo* XPS and AFM as well as the combination of both are ideally suited for studying the ALD growth initiation of Ru. Furthermore, we provided important chemical information about the initial Ru precursor adsorption on several foreign substrate materials, which will direct further investigations towards a non-inhibited Ru growth.

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### 1. Introduction

Atomic layer deposition (ALD) has emerged as a key enabling technology for the miniaturization of advanced integrated circuits and also for the implementation of new device concepts. An excellent uniformity and conformity as well as a good thickness control characterize the outstanding features of ALD [1]. Much progress has been achieved in the development of adequate ALD processes by a though time-consuming screening of various precursors behaving in dependence on the most important process parameters. However, due to technical challenges in the combination of processing and surface analysis, a fundamental understanding of the physico-chemical as well as structural surface mechanisms during the ALD has lagged behind the empirically developed ALD processes, especially in the case of ultra-thin metallic films [2].

This study intends to close this gap for the example of ruthenium's thermal-activated ALD. Aaltonen et al. [3] as well as Elliott [4] have already pointed out a special reaction mechanism during

the linear Ru-on-Ru film growth regime for a variety of organometallic precursors in conjunction with molecular oxygen. They have suggested the penetration of oxygen into the sub-surface region of the as-deposited Ru film during  $\text{O}_2$  exposures; and the subsequent complete consumption of this superficially incorporated oxygen during Ru precursor pulses.

However, the initial ALD growth of Ru on foreign substrate materials has been reported to occur non-spontaneously with a substantial incubation period [5]. Thus, the growth initiation and the transition to the linear Ru-on-Ru film growth regime are in the focus of this paper, also concerning the adsorption of the Ru precursor molecule on different initial substrate materials.

### 2. Experimental details

We investigated the thermal-activated ALD of Ru from [(ethylcyclopentadienyl)(pyrrolyl)ruthenium(II)], abbreviated as ECPR, and molecular oxygen. An ALD process from the same Ru precursor on HF-etched Si,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ , and TiN substrates has already been reported by Kukli et al. [6]. However, we developed our corresponding Ru ALD process by *in-situ* real-time spectroscopic ellipsometry

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**Table 1**

Process parameter set for the thermal-activated ALD of Ru from ECPR and O<sub>2</sub>, which was especially optimized in terms of the linear Ru-on-Ru film growth regime [7] and which was applied in this study for the initial ALD growth as well.

|                             |           |
|-----------------------------|-----------|
| ECPR bubbler temperature    | 80 °C     |
| ECPR pulsing time           | 5/7 s     |
| Ar carrier gas flow         | 50 sccm   |
| O <sub>2</sub> pulsing time | 10 s      |
| O <sub>2</sub> gas flow     | 200 sccm  |
| Ar purging time             | 20 s each |
| Ar purging gas flow         | 1000 sccm |
| Substrate temperature       | 255 °C    |
| Total process pressure      | 200 Pa    |

(SE) as recently described in Ref. [7]. There, any non-ideal effects from the starting substrate material were prevented by coating a closed Ru film prior to the process parameter variations. Thus, we ensured a process optimization in terms of the linear Ru-on-Ru film growth regime. Table 1 summarizes the corresponding process conditions, which were applied in this study for ALD growth initiation as well. The Ru films were deposited in a top-injection ALD reactor from FHR Anlagenbau GmbH that can be evacuated to a base pressure in the range of 10<sup>-4</sup> Pa. During the ALD processes, the total pressure was controlled to 200 Pa and the samples were heated to a surface temperature around 255 °C as determined by spectroscopic ellipsometry [8]. The production of pure Ru films without any oxygen incorporation in the bulk film was verified both by an absence of the O 1s signal and by a well-defined Ru 3d double peak when performing XPS after Ru precursor pulses (data not shown here).

The ALD growth of Ru was investigated on three different initial substrates: bulk silicon, a 20 nm aluminum oxide film and a 30 nm tantalum nitride film. These foreign substrate materials differed in their functional groups, which terminated the surface after a pre-treatment procedure or after the production of the respective film. The preparation and the associated surface properties of the starting substrates are summarized in Table 2.

The monocrystalline Si was pre-cleaned by dipping in VLSI-grade acetone, dipping in VLSI-grade isopropanol and rinsing with deionized water for two minutes each. Afterwards, the Si sample was etched in 0.5% hydrofluoric acid for two minutes, rinsed with deionized water again and blown dry by pure nitrogen. No fluorine residues, but ambient carbon contaminations were found at the initial Si surface by X-ray photoelectron spectroscopy (XPS).

The Al<sub>2</sub>O<sub>3</sub>(C) film was deposited by ALD from [trimethylaluminum] and water in an attached ALD-chamber ending with a water pulse. Thus, the Al<sub>2</sub>O<sub>3</sub>(C) surface was assumed to be terminated by hydroxyl groups [9]. The following transfer of the sample into the Ru reactor proceeded under a high vacuum of 10<sup>-5</sup> Pa.

The TaN<sub>x</sub>(O, C) film was deposited *in-situ* prior to the Ru experiments by ALD from [tertiarybutylimino, tris(diethylamino)tantalum] and ammonia [10] ending with an ammonia pulse. Hence, the TaN<sub>x</sub>(O, C) surface was assumed to be terminated by amino groups [11]. Sufficient argon purging separated the TaN from the subsequent Ru ALD process.

The *in-vacuo* preparation of the Al<sub>2</sub>O<sub>3</sub>(C) and TaN<sub>x</sub>(O, C) films enabled a Ru deposition on functionalized surfaces without any ambient contamination. A possible influence of carbon contaminations inside the *in-vacuo*-prepared ALD films had to be neglected for this study.

As previously described by Schmidt et al. [10] and Strehle et al. [12], our ALD-tool is attached to an ultra-high vacuum surface analytical system Multiprobe<sup>®</sup> from Omicron Nanotechnology GmbH with the possibility of X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) among others. Like in a similar study [13], we transferred an investigated sample between the

**Table 2**

Preparation and surface properties of the investigated initial substrate materials.

| Substrate                          | Preparation   | Surface properties   |
|------------------------------------|---|--|
| Si                                 | <i>ex-situ</i> : 2 min in acetone; 2 min in isopropanol; rinse with deionized water; drying with N <sub>2</sub> ; 2 min in 0.5% hydrofluoric acid; rinse with deionized water; drying with N <sub>2</sub> | H-terminated; with ambient contamination                   |
| Al <sub>2</sub> O <sub>3</sub> (C) | <i>in-vacuo</i> : in an attached ALD chamber; 180 ALD cycles with TMA and H <sub>2</sub> O at 250 °C; on silicon with native dioxide  | OH-terminated; without ambient contamination               |
| TaN <sub>x</sub> (O, C)            | <i>in-situ</i> : in the same deposition chamber; 500 ALD cycles with TBTDET and NH <sub>3</sub> at 300 °C [9]; on silicon with native dioxide   | NH <sub>2</sub> -terminated; without ambient contamination |

deposition chamber and the surface analysis system without breaking a high vacuum in the range of 10<sup>-5</sup> Pa and thus with negligible alteration of the sample after applying one ALD half-reaction or a number of cycles (*quasi-in-situ* or *in-vacuo* analysis).

XPS was used to analyze chemical states and the composition of the surface. The present XPS investigations were operated with a non-monochromatic Al-K $\alpha$  X-ray source. Thus, the photoelectrons were excited by a radiation of 1486.6 eV. Those photoelectrons that were emitted from the sample surface under an angle of 45° were detected in a hemispherical analyzer according to their kinetic energy. The constant analyzer pass energy (CAE) was set to 30/50 eV. The evaluation and synthesis of the acquired XP spectra were performed with the XPS analyses software UNIFIT 2011 [14]. The satellites and a Shirley background were subtracted from the measured spectra. UNIFIT 2011 uses the curve fitting algorithm of Marquardt for peak synthesis.

The surface roughness was determined over an area of 500 × 500 nm with a non-contact AFM.

### 3. Results

#### 3.1. Ruthenium growth on a hydrogen-terminated silicon surface

In this first part, we focus on the ALD growth of Ru starting on a H-terminated Si surface. Fig. 1a shows the original XP spectra in a range of the binding energy from 456 to 468 eV indicating an arising Ru 3p<sup>3/2</sup> signal for progressing ALD cycle numbers. After subtraction of a Shirley background, the increasing area under the Ru peak is plotted over the cycle number in Fig. 2a as the green curve with triangles.

This graph shows three distinct growth regimes: an incubation period of about 20 cycles, where only a very slight Ru nucleation occurred; a transition period until around the 100th ALD cycle; and the homogeneous Ru-on-Ru film growth regime, where the Ru 3p<sup>3/2</sup> XPS signal saturates as the film thickness exceeded the mean free path of the emitted photoelectrons. In the latest regime, no signal from the Si substrate was detected and a homogeneous ALD growth was assumed. According to Puurunen et al. [15], this division into three distinct growth regions indicated a substrate-inhibited ALD growth.

Fig. 1b prints the spectra of X-ray-excited O 1s photoelectrons measured after O<sub>2</sub> pulses in the progress of the ALD cycle number. This also pointed out the incubation time until the 20th ALD cycle; and it revealed the emersion of two different oxygen binding states in the transition regime (between the 20th and around 100th ALD cycle). For an exemplary XP spectrum after the 50th ALD cycle, Fig. 1c demonstrates the deconvolution of the O 1s peak into its two components: The first binding state is located at a binding en-

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