In-situ and in-vacuo studies on area selective atomic layer deposited ruthenium films on silicon and silicon oxide

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We present a thermal activated inherent area selective atomic layer deposition (*thALD*) of ruthenium (*Ru*) on crystalline silicon (*cSi*) wafer and silicon oxide (SiO_2) interfaces.
The selective deposition is based upon the inhibited nucleation of ruthenium on oxide surfaces such as SiO_2 compared to Si and metal surfaces. ThALD ruthenium (5-20 nm thick) deposited with the organometallic precursor ECPR [(ethylcyclopentadienyl)(pyrrolyl) ruthenium(II)] and molecular oxygen [1, 2] on 4 inch silicon [100] wafers with a pattern of cSi dipped by diluted hydrofluoric acid (*HF*), and native silicon oxide (1.8 nm).
In our experiments, the pattern on the wafer was created by lithography with AZ® 5214 E resist. A dip with 0.5% HF (30 s) was used to remove the native oxide film on cSi and to create a hydrogen-terminated surface. Immediately afterwards, the resist was stripped by a treatment with acetone, 2-propanol, and clean water (conductivity 0.05 µS/cm). After drying, the wafer was transferred into ALD tool for deposition within less than 5 minutes.
As shown in [2-4], the initially incubating and nucleation periods strongly depend on the deposition temperature. On HF-dipped cSi after a nucleation period of 10 ALD cycles a steady-state Ru-on-Ru(Ox) growth with a GPC of ca. 0.9 Å was observed (Fig. 1) at 180 °C. In the linear steady-state region the GPC was nearly independent on the deposition temperature [2]. On native SiO_2, only isolated islands of Ru were formed in negligible quantity after 150-180 ALD cycles, consisting of non-stoichiometric Ru / Ru(Ox). Here, growth started after 180 ALD cycles, whereas on HF-dipped Si a 16 nm thick Ru film (Rs= 14,2 Ω/□; ρ= 22,72 µΩ*cm) has been deposited already (Fig. 2). A higher quality of selectivity became be achieved by combining ALD with selective etching using an O_2 or O_3 purge after a certain number of ALD cycles (Fig. 3). As we demonstrated earlier [1, 2], purge steps with molecular hydrogen (H_2) during Ru-ALD can prevent blister formation.

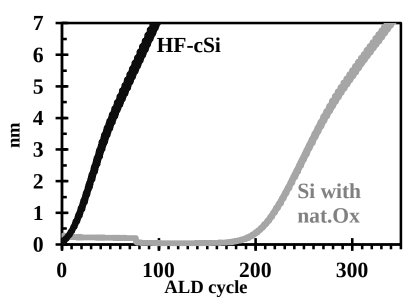

Fig. 1: In-situ real-time spectroscopic ellipsometry of selective ALD a) HF dipped cSi b) Si with nat. SiO_2; deposition temp. 180 °C

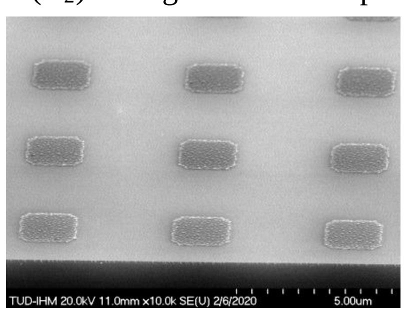

Fig. 2: SEM images of 16 nm Ru [180x Ru (ECPR-O_2) thALD; 180 °C] on Si wafer with a pattern of crystalline silicon dipped by HF and untreated native silicon dioxide (1.8 nm) - Ru grew on cSi only

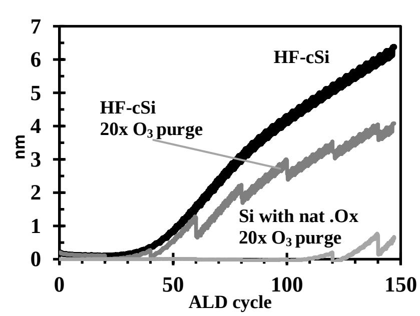

Fig. 3: In-situ real-time spectroscopic ellipsometry of selective ALD with an additional O3 Purge after 20 ALD Cycle; Substrates: a) HF dipped cSi; b) HF dipped cSi and c) Si with nat. SiO_2

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