Development of a Cobalt Atomic Layer Deposition Process using $Co_2(CO)_6HC{\equiv}CC_5H_{11}$ as Precursor

Low-Temperature PEALD of Metallic Cobalt

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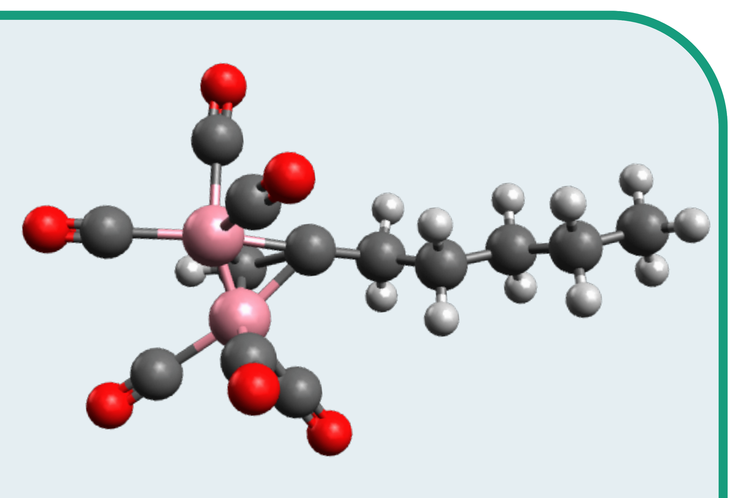
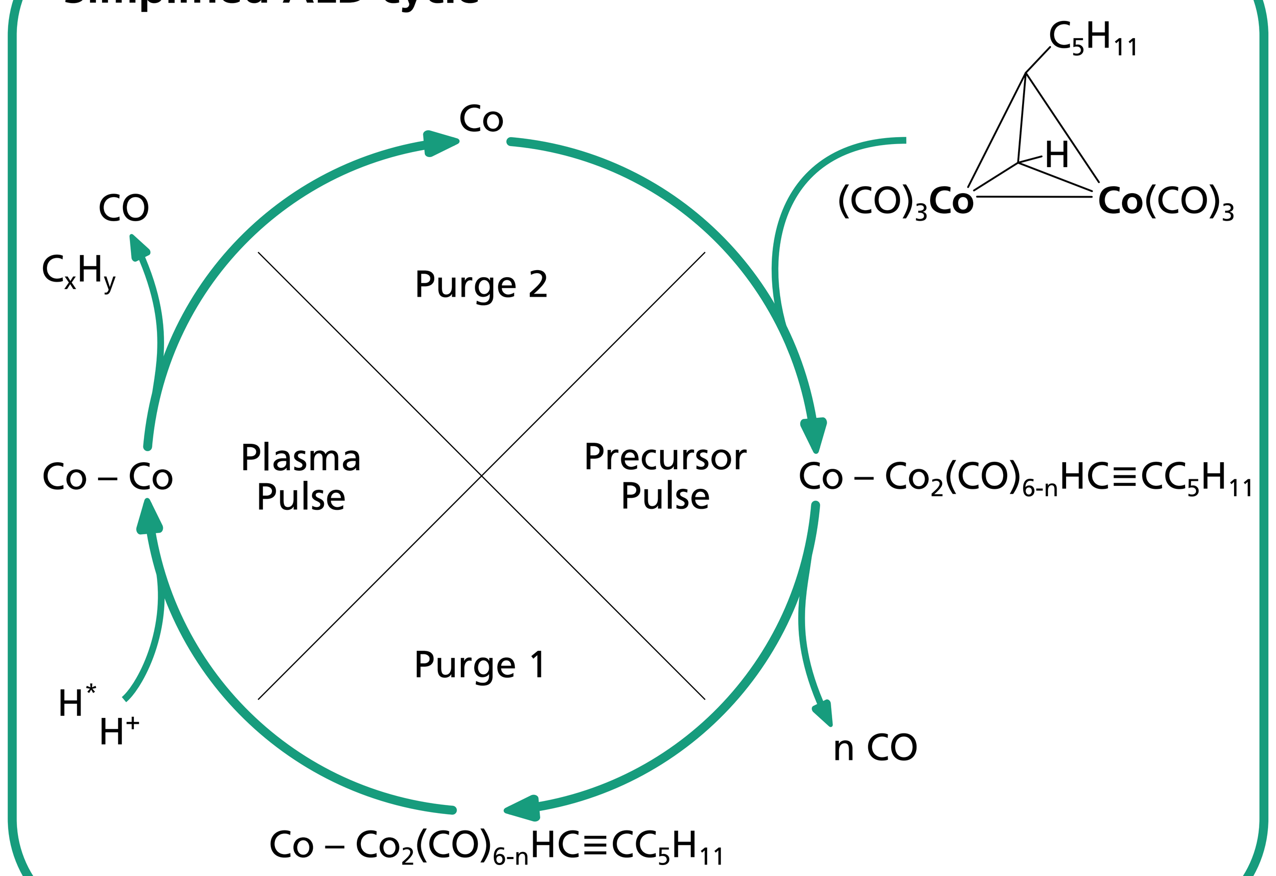
Atomic Layer Deposition of Metallic Cobalt

The deposition of ultra-thin metallic cobalt films is an ongoing topic of research. Cobalt is a promising candidate to replace copper in modern interconnect systems with feature sizes below 20 nm. Another application is the use of metallic cobalt in the nanometre scale in magnetic sensors. Especially the atomic layer deposition (ALD) gives the opportunity to deposit thin films homogeneously even in structures with a high aspect ratio or small feature sizes.
Here, we present the development of a low-temperature plasma-enhanced ALD process with an ALD window in the temperature region between 50 °C and 110 °C. For the deposition of metallic cobalt we used dicobalt-hexacarbonyl-1-heptyne $[Co_2(CO)_6HC{\equiv}CC_5H_{11}]$ as precursor. The synthesis and the basic characteristics had been described by Georgi et al.[1] The process development took place in a *scia Atol 200* machine from scia Systems GmbH. The precursor was evaporated by bubbling with Argon carrier gas. The second precursor pulse was a hydrogen plasma pulse. Both pulses were separated by purging with pure Argon. The estimated reaction steps during the ALD cycle is shown on the right side. These assumptions base on density functional theory simulations giving the most probable reaction pathway. The precursor adsorbes on the cobalt surface and the -CO groups will be released partially. In the second step, the hydrogen radicals react with the surface bound heptyne group forming volatile hydrocarbons. The remaining -CO groups will be released as well. In that way only the cobalt will remain on the surface and the next ALD cycle can start.



3D sketch of $[Co_2(CO)_6HC{\equiv}CC_5H_{11}]$

Simplified ALD cycle

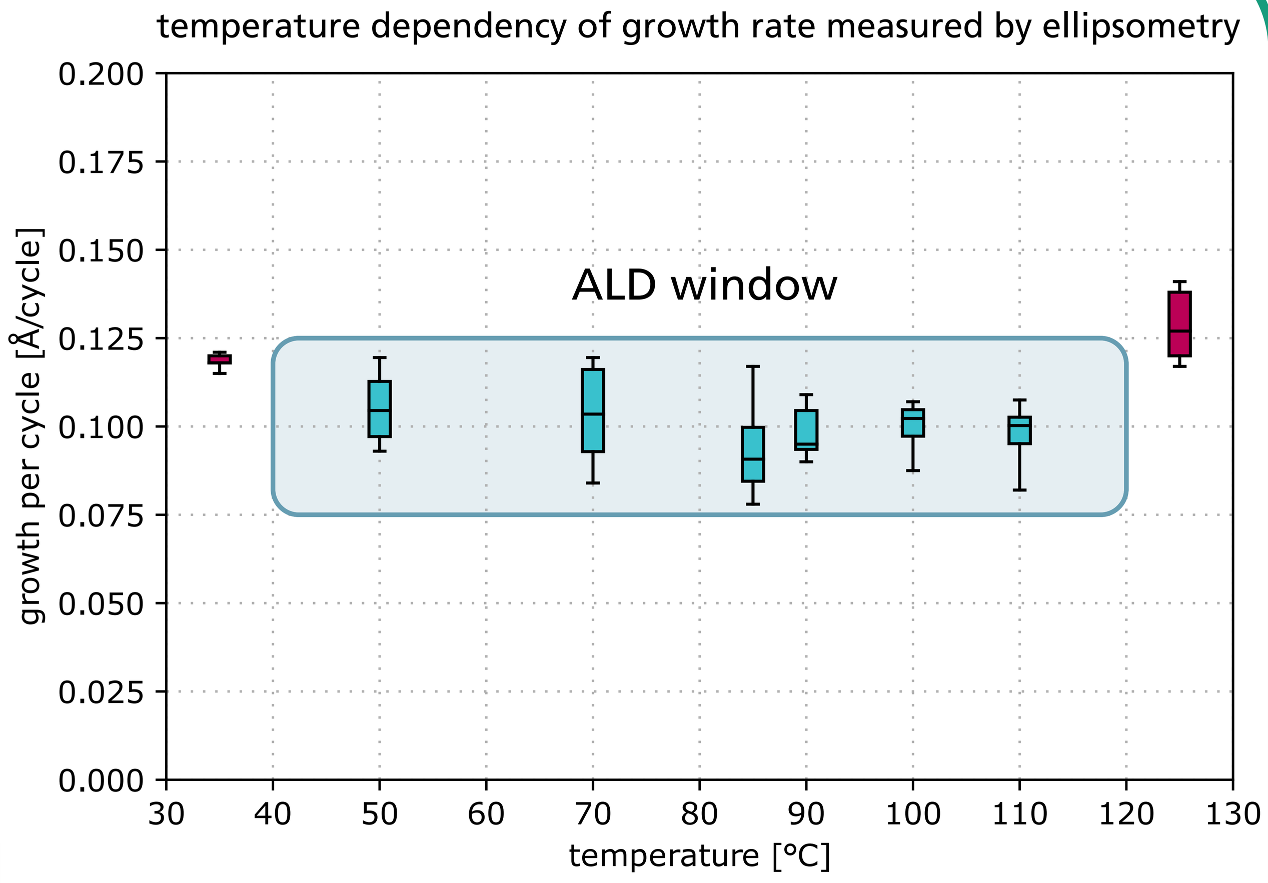


Equipment:
scia Atol 200
PEALD tool for 200 mm wafer

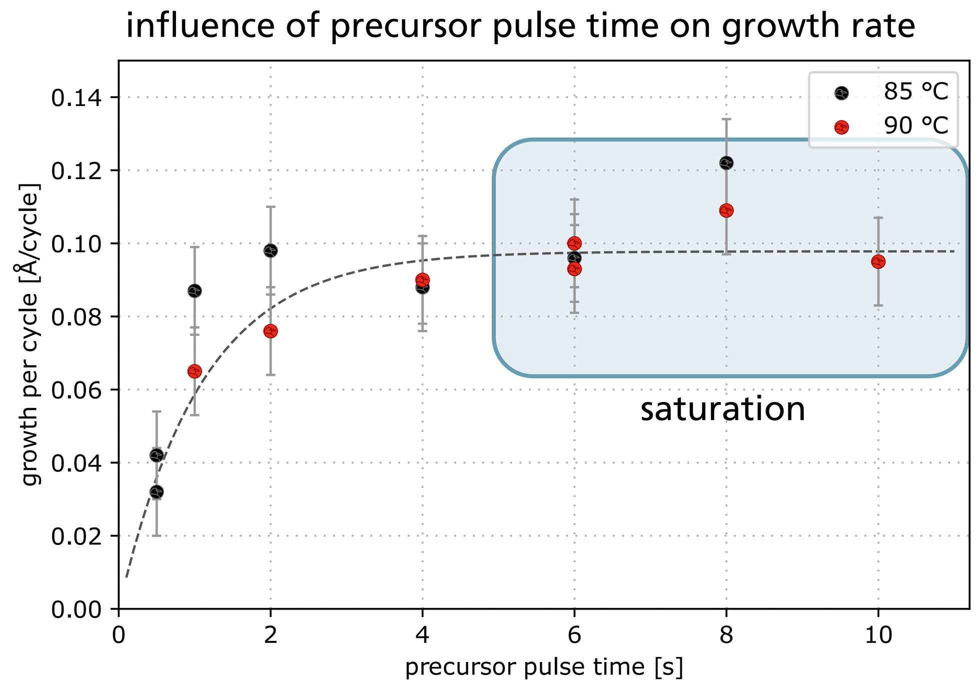
The ALD process

We investigated the temperature behaviour of the ALD process. The precursor decomposes at temperatures of 125 °C and above. Temperatures of 35 °C and below lead to an incomplete removal of the precursor ligands during the hydrogen plasma step. In the temperature range between 50 °C and 110 °C a stable growth rate of approximately 1 Å/cycle could be observed. This temperature region was identified as the ALD window.
The saturation behaviour had been analysed for various temperatures. An exponential decay approximation shows that the surface saturates after a precursor pulse of 5 s.

temperature dependency of growth rate measured by ellipsometry



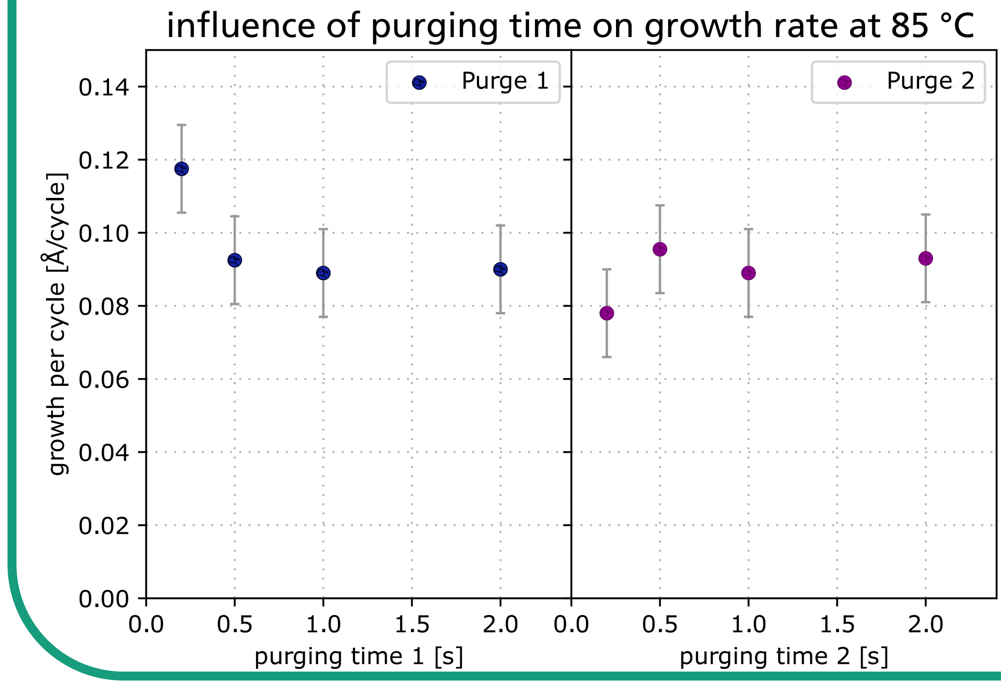
influence of precursor pulse time on growth rate



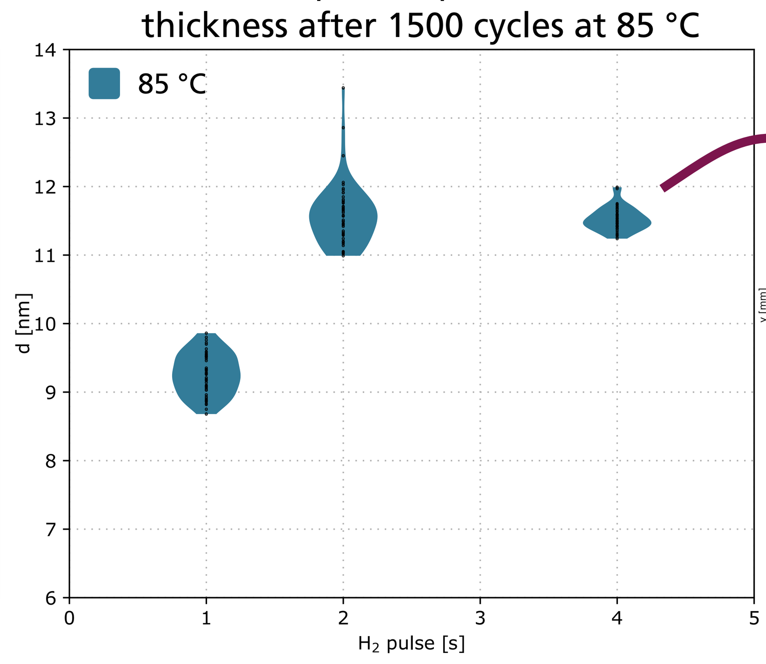
The purging after the precursur pulse (Purge 1) has to be at least 0.5 s long to remove the cobalt precursor completely. The purging after the plasma step (Purge 2) can be 0.2 s long.

The influence of the H_2 plasma pulse duration had been analysed for processes with 1500 cycles at 85 °C. The film thickness distribution had been measured by spectroscopic ellipsometry on 50 points on the wafer surface using a spiral pattern. The plasma pulse has to be at least 2 s long. Longer plasma pulse duratinos will result in a more homogeneous film.

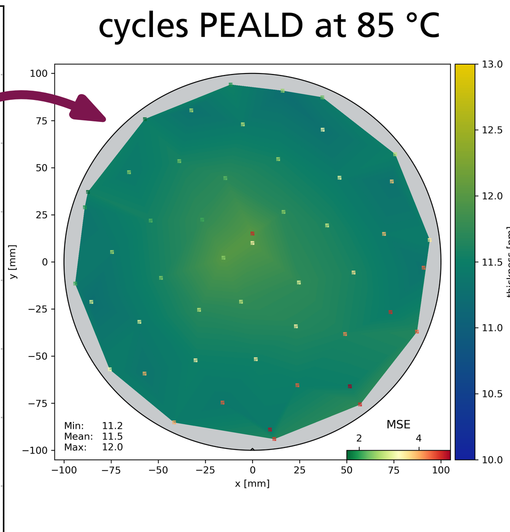
influence of purging time on growth rate at 85 °C



influence of plasma pulse time on film thickness after 1500 cycles at 85 °C



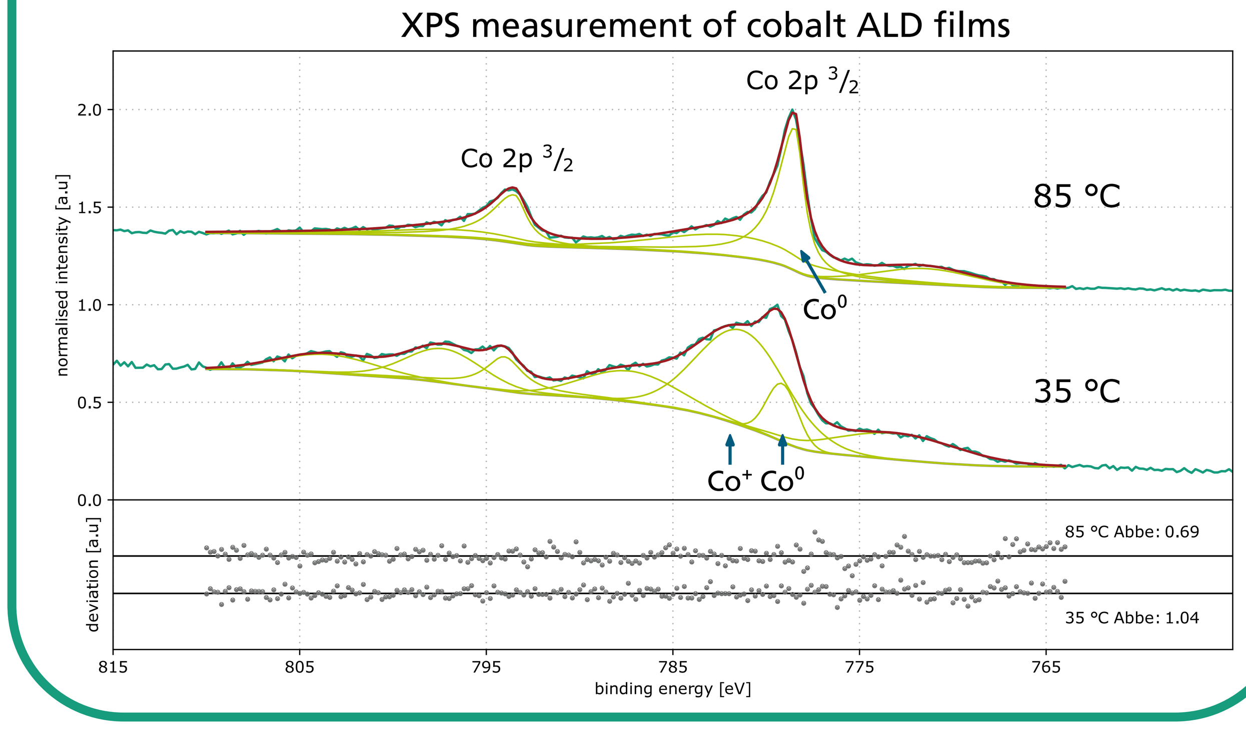
film thickness distribution on 200 mm wafer after 1500 cycles PEALD at 85 °C



Film Analysis

The deposited cobalt films had been analysed by ex situ X-ray photoelectron spectroscopy measurements. Films which were deposited at 35 °C show a significant amount of carbon and oxygen contaminations and here the cobalt is in oxidised state. This implies an insufficiant reaction with the precursor ligands during the plasma step. Films which are deposited at temperatures within the ALD window show low contaminations and the deposited cobalt is completely in metallic state.

XPS measurement of cobalt ALD films



Conclusion

We could successfully develop a 200 mm wafer PEALD process for the deposition of metallic cobalt by use of dicobalt-hexacarbonyl-1-heptyne as precursor. We could show that hydrogen plasma is a suitable reduction agent to remove the precursor ligands and to create a metallic cobalt film. The process operates at low temperatures between 50 °C and 110 °C. The growth rate within this ALD window is approximately 1.0 Å/cycle.

[1] C. Georgi, A. Hildebrandt, T. Waechtler, S. E. Schulz, T. Gessner, and H. Lang, "A cobalt layer deposition study: Dicobaltatetrahedranes as convenient MOCVD precursor systems", J. Mater. Chem. C, vol. 2, no. 23, pp. 4676–4682, 2014, doi: 10.1039/c4tc00288a.

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