Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

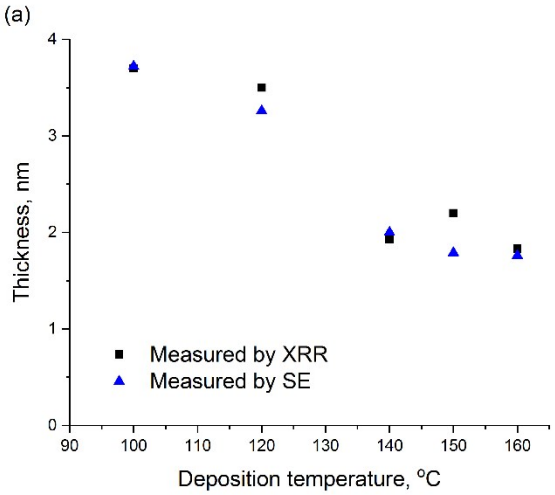
Selective Electroless Deposition of Cobalt using Amino-terminated SAMs.

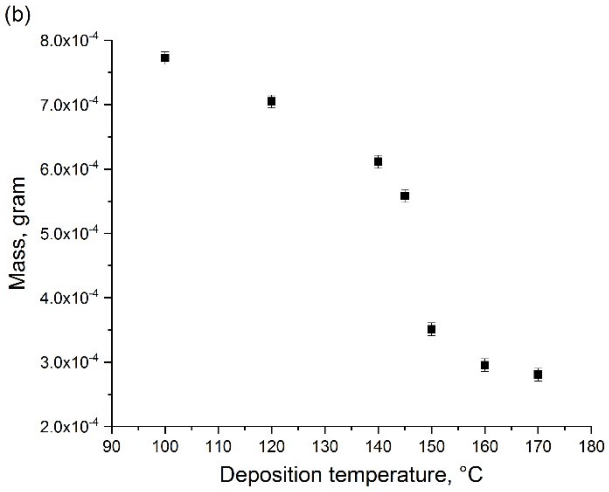
Ivan Zyulkov*[a,b], Silvia Armini [b], Karl Opsomer [b], Christophe Detavernier [c], Stefan De Gendt [a,b]

[a.] *KU Leuven, Department of Chemistry, Faculty of Science, 3001 Leuven, Belgium.*
[b.] *Imec, Kapeldreef 75, 3001 Leuven, Belgium.*
[c.] *Ghent University, Department of Solid State Sciences, CoCooN, Krijgslaan 281 - S1, 9000 Ghent, Belgium.*

Optimization of the DETA SAM deposition process

SAMs grafting was performed at various temperatures with a deposition time of 1 hour in order to investigate the impact of the deposition temperature on the SAMs density. A 100 µl droplet of precursor was placed in the deposition chamber on a glass slide. Thickness of the SAM layer was measured by SE and XRR. A one-layer model based on the Cauchy approximation was used to fit the spectra collected in the wavelength range of 400–800 nm. Results of the data fitting are shown in Figure S1a:





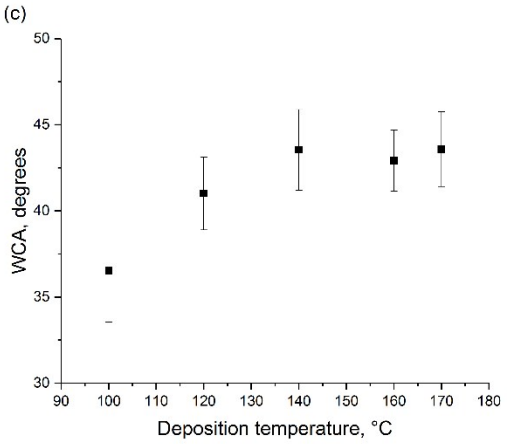


Figure S1. SAM (a) thickness measured by XRR and SE, (b) mass and (c) WCA as a function of SAM deposition temperature.

According to Figure S1a, the thickness of the SAM layer deposited at 100 ºC is around 3.7 nm. The length of the DETA molecule is reported to be ~ 1.4 nm[1,2], therefore it can be concluded that multilayers of DETA are formed. Since DETA molecule has three methoxy groups, it is possible that SAMs crosslinking occurs due to the reaction of the hydrolysed methoxy groups with each other. However, the thickness of SAMs decreases if higher deposition temperature is used and approaches ~ 1.9 nm when the deposition temperature reaches 140 ºC. Decrease of the SAM thickness is probably caused by lower water concentration in the deposition chamber if higher deposition temperature is used, which results in a lower possibility of disordered cross-linking of the SAMs molecules in the favour of DETA molecules reaction on the wafer surface. SAM thickness decrease at high deposition temperature can also be due to the fact that the deposition chamber is constantly pumped to maintain the pressure of 10 mTorr. As a result, SAMs precursor can be evaporated fast at higher temperature and evacuated from the chamber by the pump, which will decrease the total dose of the precursor. In order to compare the amount of the organic material on the samples deposited at various temperatures, the mass of the 300 mm wafers was measured before and immediately after the silanization. The mass of the organic films as a function of the deposition temperature is shown in Figure S1b. In order to have a first assessment of the SAMs properties, the surface wettability was measured by the static WCA measurement. As can be seen in Figure S1c, SAM WCA increases simultaneously with the film densification, while it is close to zero degrees after UVO_3 clean. The WCA value approaches 43 degrees at 140 ºC, which has a good correlation with literature data on WCA of amino-terminated SAM layers.[1] At a result, it can be concluded that 140 ºC is a good deposition temperature to achieve high surface density of amino functionalities, while minimizing the SAM thickness.

To investigate Pd chemisorption on DETA SAM surface, the samples coated with DETA SAM were immersed into the $PdCl_2$ solution for 2 minutes. After the deposition and rinsing in DIW, Pd areal density was measured by RBS as shown in Figure S2a. Areal density of the SAM molecules was calculated based on the mass of the SAM layer and molecular weight of the DETA precursor (265.43).

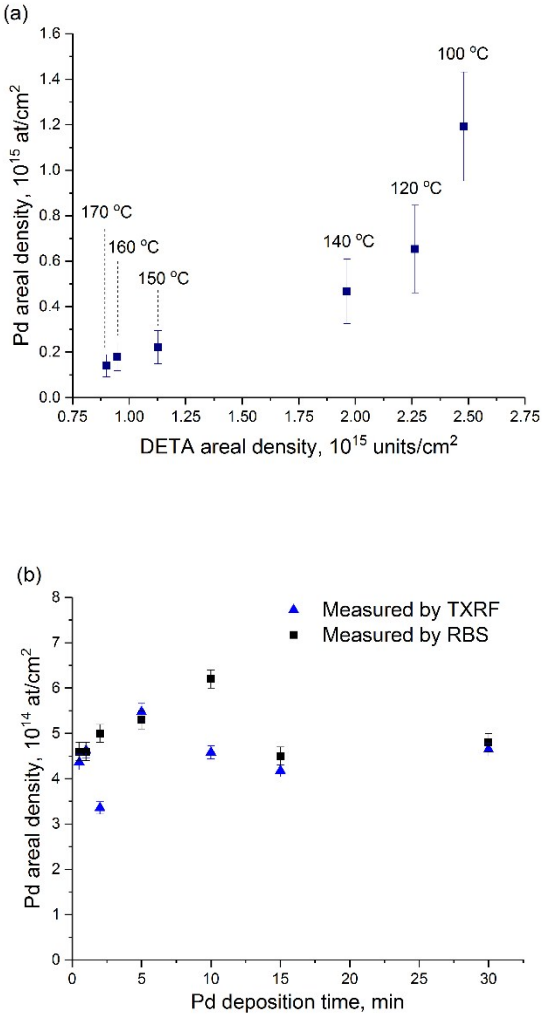


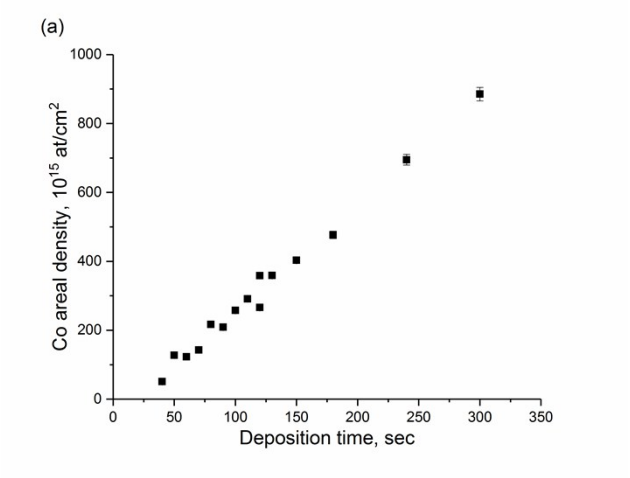
Figure S2. RBS Pd areal density (a) as a function of the DETA areal density, (b) Pd areal density, measured by RBS and TXRF as a function of the Pd deposition time.

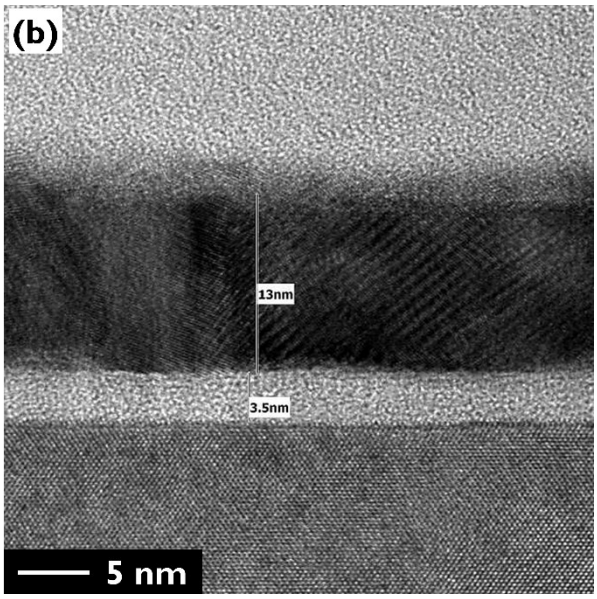
According to several studies[3–5], Pd from acidic $PdCl_2$ solution interacts with surface amino groups. Therefore, high Pd concentration is expected for a SAM layer with high surface density of amino functionalities. As it can be seen in Figure S2a, the Pd areal density decreases with increasing SAM deposition temperature, which is unexpected since SAM amino groups density is

proportional to the SAM deposition temperature (Figure S1c). However, the Pd areal density is proportional to the number of DETA molecules per square centimetre, as it can be seen in Figure S2a. Taking into account that SAMs are forming multilayers when the deposition temperature is below 140 ºC, it can be concluded that Pd is attached not only to the surface amino groups, but it is also reacting with the secondary amino groups in the DETA layer.

As it was described in the introduction, Pd is used as a catalyst for Co ELD, therefore areal density of Pd close 10^{14} at/cm^2 to 10^{15} at/cm^2 is desired to provide a uniform Co nucleation and strong Co adhesion to the substrate. Based on Pd areal density in Figure S2a and SAM thickness shown in Figure S1a, it can be concluded that SAM deposition temperature of 140 ºC should be used as a trade-off between Pd areal density and SAM thickness. To confirm that the Pd chemisorption is not limited by the Pd deposition time, samples with SAMs deposited at 140 ºC were dipped into $PdCl_2$ solution for a various amount of time. The areal density of the Pd atoms was quantified by RBS and TXRF to get more statistic and to perform a cross-check between two measurement techniques, as shown in Figure S2b. Pd areal densities measured by TXRF and RBS show a good matching of values with a maximum deviation not exceeding of $0.5 \cdot 10^{14}$ at/cm^2. At the same time, no correlation was observed between the Pd areal density and Pd deposition time, which suggests that Pd chemisorption reaction goes into completion very fast. The average Pd areal density observed on samples functionalized by DETA SAMs at 140 ºC is estimated to be $4.5 \cdot 10^{14}$ at/cm^2 ± $0.5 \cdot 10^{14}$ at/cm^2.

Co areal density as function of the deposition time as measured by RBS:





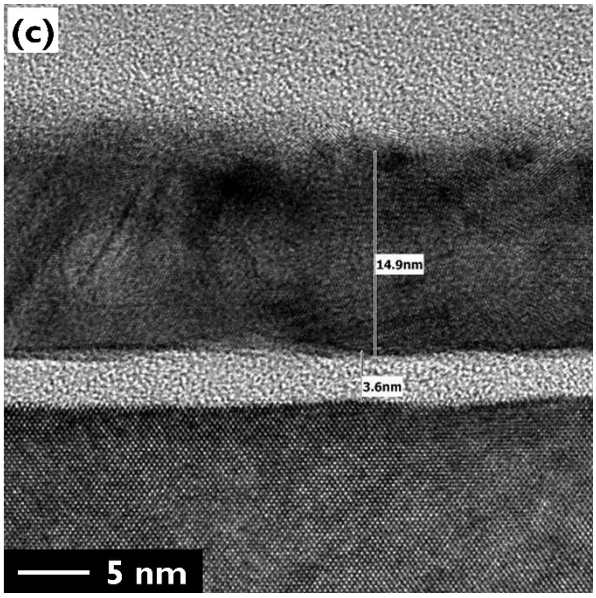


Figure S3. (a) RBS Co areal density after annealing, (b) and (c) cross-sectional TEM images of the annealed Co film deposited within 55 seconds and 60 seconds ELD time.

In-situ XRD study of Co recrystallisation, heating profile:

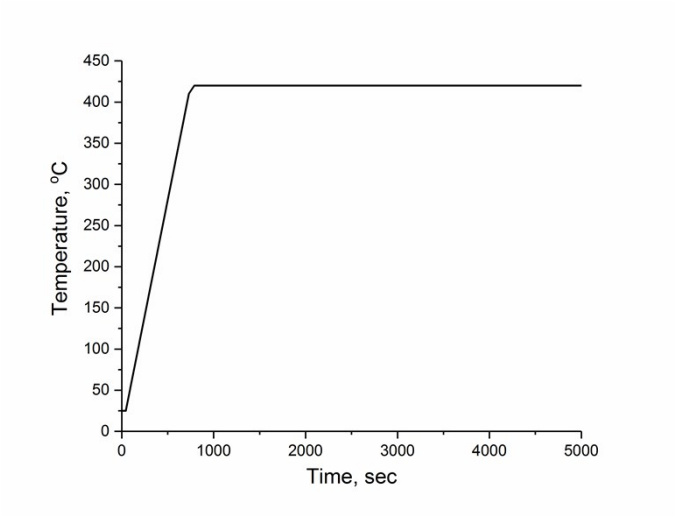


Figure S4. Temperature profile as the function of the annealing time.

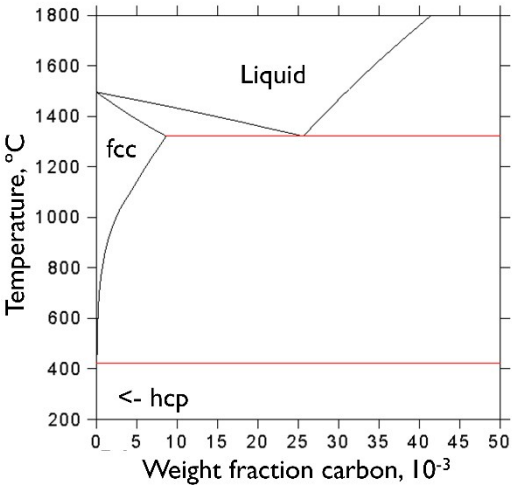


Figure S5. Co-C phase diagram. Adopted from A. Fernandez Guillermet.[6]

Calculated resistivity of ELD Co:

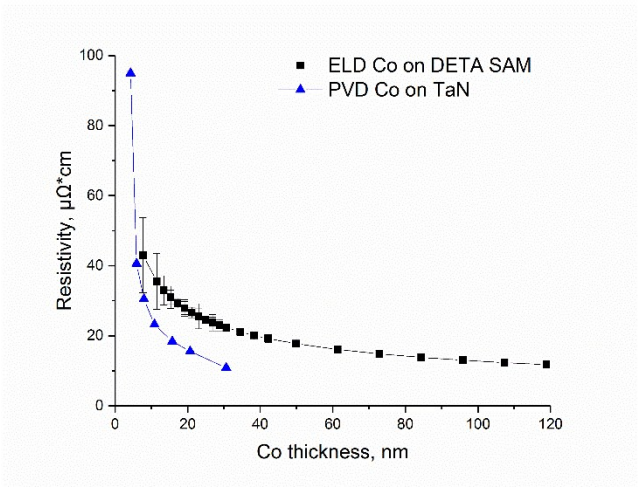


Figure S6. ELD Co resistivity as a function of the film thickness.

References:

1 Y. Sun, A. R. Negreira, J. Meersschaut, I. Hoflijk, I. Vaesen, T. Conard, H. Struyf, Z. Tokei, J. Boemmels, M. Moinpour, S. De Feyter and S. Armini, *Microelectron. Eng.*, 2017, **167**, 32–36.

2 A. Hozumi, Y. Yokogawa, T. Kameyama, H. Sugimura, K. Hayashi, O. Takai, A. Hozumi, Y. Yokogawa and T. Kameyama, *J. Vac. Sci. Technol. A*, 2005, **1812**, 10–15.

3 W. J. Dressick, C. S. Dulcey, J. H. Georger, G. S. Calabrese and J. M. Calvert, *J. Electrochem. Soc.*, 1994, **141**, 210.

4 S. L. Brandow, *J. Electrochem. Soc.*, 1995, **142**, 2233.

5 H. Kind, A. M. Bittner, O. Cavalleri, K. Kern and T. Greber, *J. Phys. Chem. B*, 1998, **102**, 7582–7589.

6 A. F. Guillermet, *Z. Met.*, 1987, **78**, 700–709.