

Cobalt and Ruthenium drift in ultra-thin oxides

D. Tierno*, O. Varela Pedreira, C. Wu, N. Jourdan, L. Kljucar, Zs. Tókei, K. Croes

IMEC, Kapeldreef 75, 3001 Leuven, Belgium

ABSTRACT

Cobalt (Co) and ruthenium (Ru) have been proposed for novel metallization schemes to replace copper in next generation BEOL systems that will use ultra-thin oxide layers. Using TDDB measurements performed on planar capacitors we evaluated the performances of the two metals: both CVD Co and CVD Ru are affected by metal drift, differently to previously reported results for ALD and PVD Ru that showed no sign of metal drift. We believe that not oxide scaling, but the deposition conditions used for our CVD process are responsible for the different behaviour of Ru. In particular, the CVD precursors used for Ru deposition lead to the incorporation of impurities that made the Ru bonds easier to break and thus CVD Ru is more susceptible to ionization processes occurring at the metal/dielectric interface. Moreover, our data show also an impact of the SiO₂ deposition technique on these processes because PECVD and PEALD lead to different oxide surface conditions. Finally, an increase in acceleration factor was observed at low field values for both Co and Ru, as predicted by the filament formation and growth model, confirming the need to test BEOL systems in a wide range of test conditions for reliable lifetime estimations.

1. Introduction

The continuous scaling of features size dictated by advanced technology nodes requires the development of novel metallization approaches for both Middle-of-Line (MOL) and Back-End-of-Line (BEOL). A degradation of performances is expected to accompany the scaling of interconnects, primarily an increase in resistivity for scaled copper lines because the contribution of electron scattering to the resistivity increases as feature size decreases [1,2]. Moreover, in aggressively scaled copper systems the percentage of the interconnect line utilized by the barrier/liner increases thus further augmenting the resistance. It is established that Cu requires a barrier to avoid metal drifting into the dielectric, a phenomenon that poses a serious threat to interconnect reliability. To address such issues, alternative metallization schemes with thinner barrier/liners have been proposed to maximize the volume of the metal line [3,4]. Alternatively, Adelman et al. [5] suggested that metals with melting temperatures higher than Cu, such as Ru and Co, might be less sensitive to electromigration and metal drift. Moreover, Dutta et al. [6,7] have shown that the resistivity of both Co and Ru is less sensitive to scaling and in features smaller than 10 nm their resistivity is comparable to Cu. Hence, Ru and Co are both promising candidates for ultra-scaled interconnect systems. In particular, Ru is expected to be suitable for barrierless integration schemes. In fact, in a previous study, Varela Pedreira et al. [8] have shown that Co drifts in thick SiO₂ whereas no metal drift has been observed for ALD and PVD Ru for the same test conditions (SiO₂ thickness, field, temperature, etc.).

In this study the reliability of Co and Ru, both deposited by Chemical Vapor Deposition (CVD), in ultra-thin SiO₂ layers is evaluated. In fact, in ultra-thin oxides (~10 nm), that will be used in next generation BEOL systems, different conduction mechanisms regulate the current driven degradation of oxide films; as the thickness is reduced direct tunnelling rather than the Fowler-Nordheim regime becomes relevant [9]. We show that metal deposition method and oxide surface condition are influencing the behaviour of Co and Ru. Moreover, at low fields, intrinsic breakdown competes with metal-drift induced failure as ultimate failure mechanism, according to the metal formation and growth model proposed by Wu et al. [10] for BEOL and MOL. The experimental data confirm that for a proper characterization of the system, a wide range of test conditions are necessary.

2. Experimental

2.1. Test vehicle and method

Metal-Insulator-Metal (MIM) planar capacitors (p-caps) [11] were used to investigate metal drift induced failure. A schematic of the test vehicle is shown in Fig. 1a. Two series of devices were fabricated: 13 nm-thick SiO₂ films were deposited into 100 μm × 100 μm cavities using low-temperature Plasma Enhanced Chemical Vapor Deposition (PECVD) and Plasma Enhanced Atomic Layer Deposition (PEALD). The two techniques produce different oxide films in terms of density, impurities, etc., because of the distinct process parameters [12–14] that

* Corresponding author.

E-mail address: davide.tierno@imec.be (D. Tierno).

<https://doi.org/10.1016/j.microrel.2019.113407>

Received 13 May 2019; Received in revised form 13 June 2019; Accepted 2 July 2019

0026-2714/ © 2019 Elsevier Ltd. All rights reserved.

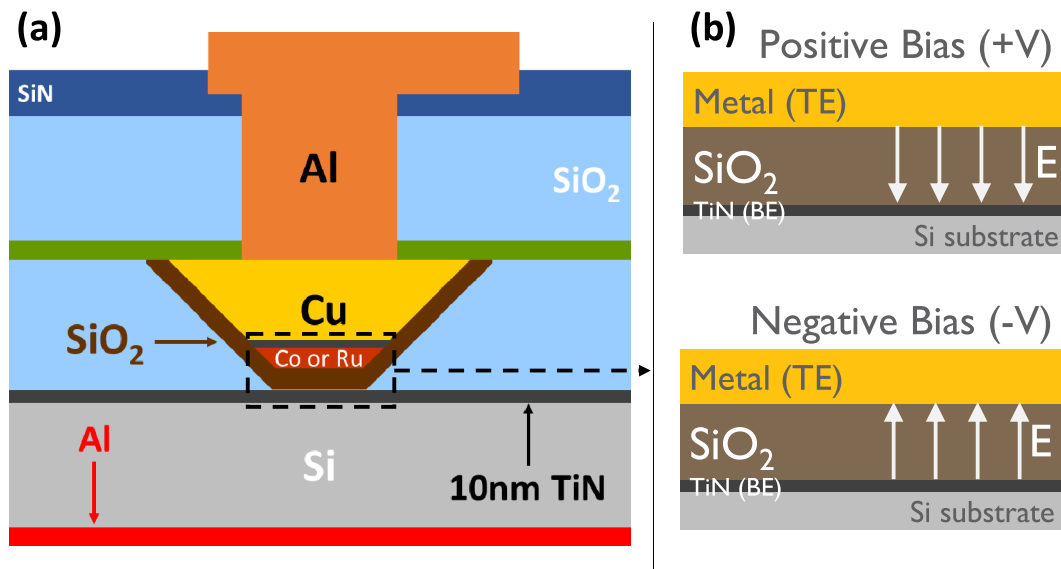


Fig. 1. (a) Schematic of a MIM p-cap. The metallization includes the Co or Ru TE (red), the TaN/Ta barrier (black) and the final Cu fill (yellow). (b) Two breakdown mechanisms can be studied using the test vehicle under different bias polarities: metal drift induced failure when a positive bias (POS) is applied to the top electrode and intrinsic breakdown when a negative bias (NEG) is used. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Dielectric constant (k) and intrinsic breakdown field (E_{BD}) for the various p-caps systems.

| Metal | SiO ₂ | k | E_{BD} [MV/cm] |
|-------|------------------|---------------|------------------|
| Co | PECVD | 3.9 ± 0.1 | -13.0 ± 0.3 |
| | PEALD | 4.8 ± 0.1 | -10.7 ± 0.3 |
| Ru | PECVD | 4.2 ± 0.0 | -12.7 ± 0.3 |
| | PEALD | 4.3 ± 0.1 | -13.3 ± 0.8 |

we expect to influence the ionization processes at the metal/dielectric interface. For the bottom electrode (BE) a 10 nm-thick TiN layer, an inert material that does not drift into the dielectric, is used. The top electrode (TE) is designed to assess metal drift with a not-fully closed TiN adhesion layer interposed between the dielectric and the metal. A 10 nm-thick layer of either CVD Co or CVD Ru was deposited and capped using a TaN/Ta layer whereas the rest of the cavity is filled with Cu to minimize deposition time. The two resulting metallization schemes were thus Co(10 nm)/TaN/Ta/Cu and Ru(10 nm)/TaN/Ta/Cu. Planar capacitors were also fabricated using 40 nm-thick PECVD SiO₂ and are used as reference. In our MIM p-caps the failure mechanism is affected by using positive and negative bias stresses for metal drift induced failure and intrinsic dielectric degradation, respectively (Fig. 1b) [11]. For this study, Time Dependent Dielectric Breakdown (TDDB) [15–17] tests were performed at 25 °C, 100 °C and 200 °C for both positive and negative stress voltages. At each temperature, various electric fields were used to stress different structures till failure; the Weibull scale parameter $t_{63.2\%}$ (TTF 63.2%) was obtained for each condition and the experimental data were fitted using the power law model ($t_{63.2\%} \sim E^{-m}$) to extract the field acceleration factor (m) [18–20]. The failure criterion was defined as an abrupt change in the leakage current. A difference in the acceleration factor extracted from TDDB

measurements for positive and negative stress voltages is considered to be a sign of metal drift, indicating different failure causes for the two polarities.

TDDB at 200 °C was used to stress the test vehicles at low fields, while maintaining a reasonable testing time ($< 10^5$ s/device). Based on the model proposed by Wu et al. [10] metal drift occurs in two different regimes. At high fields the metal filament rapidly grows into the dielectric leading to a rapid failure of the system and it is characterized by low acceleration factors. The filament formation regime, dominating at low fields, is characterized by high acceleration factors and a very steep TTF vs. E relation. The incubation time for the formation of the filament is potentially very long and it strongly depends on dielectric thickness, barrier continuity and electric field. As a consequence, even though metal drift occurs it might not be the ultimate cause of failure; at low fields it might be preceded by the intrinsic breakdown. However, only under specific test conditions such a regime could be observed; consequently, standard TDDB at 100 °C are not sufficient and TDDB at 200 °C and low stress fields are needed.

2.2. Dielectric properties

All metal-SiO₂ combinations were first characterized to extract the dielectric constant and the intrinsic breakdown field; the values, which were extracted using nominal film thicknesses (13 nm), are reported in Table 1. The p-caps with Ru metallization show similar dielectric constant and breakdown values for PECVD and PEALD SiO₂ films and are consistent with those previously reported for thicker films [8].

On the other hand, the values extracted from Co-based devices show a sizeable difference not only when compared to Ru-based devices but also when comparing PECVD to PEALD oxide. A $\sim 10\%$ deviation of the effective thickness from the nominal one (~ 1.5 nm), caused by wafer-to-wafer process variability, would account for such a variation of the extracted values.

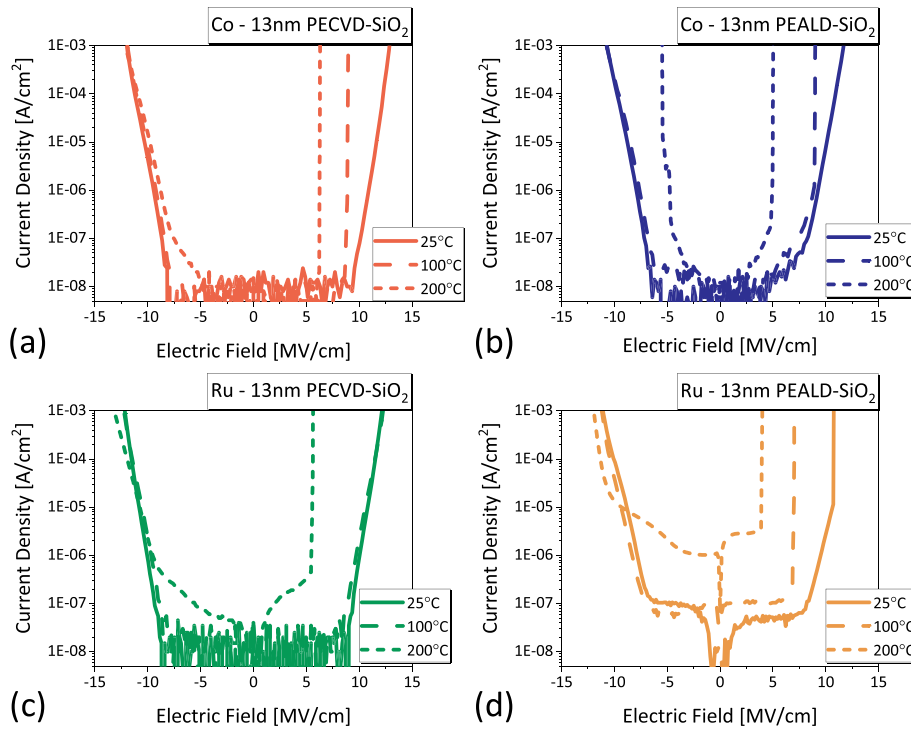


Fig. 2. Current density recorded at 25 °C, 100 °C and 200 °C before TDDB measurements for p-caps with (a) Co/PECVD SiO₂, (b) Co/PEALD SiO₂, (c) Ru/PECVD SiO₂ and (d) Ru/PEALD SiO₂.

2.3. TDDB measurements

Before performing TDDB measurements, the leakage current density was recorded on each device and the J-E curves are plotted in Fig. 2. The leakage current at low fields is approximately the same for all devices for both positive and negative applied voltages up to 100 °C. For positive stress voltages, a considerable degradation of the breakdown field with temperature is observable across the four different scenarios and it is likely induced by metal drift. PECVD oxide is less impacted than PEALD oxide for which the breakdown field is, on average, 2 MV/cm lower. The effect is visible for both Ru and Co suggesting that metal drift occurs for both metallization schemes. In addition, an increase in leakage current can be noticed at 200 °C for p-caps with PEALD oxide for both Ru and Co metallization schemes. Such a variation is partially caused by thermally activated defects that affect PEALD SiO₂ more than PECVD SiO₂. On the other hand, the variation of the intrinsic breakdown field as temperature is increased is negligible for all cases except for the Co/PEALD SiO₂ (Fig. 2b), consistently with the results reported in the previous section. The role played by the oxide is discussed in detail in the next section.

The TDDB data gathered at 25 °C, 100 °C and 200 °C for all the devices are plotted in Fig. 3. Consistently with what was observed in the J-E curves discussed above, the intrinsic breakdown (NEG) changes very little with temperature and, as expected, it is independent of the metal used for the TE. A more diverse scenario was instead observed for positive stress voltages with no match between positive and negative data points, hence confirming that metal drift occurs not only for Co, for which it was expected, but also for CVD Ru, differently to what previously reported for ALD and PVD Ru [8].

It should be emphasized that a different deposition technique as well as thinner oxide films were used for this study. We believe that CVD process conditions are responsible for the different behaviour here observed for CVD Ru with respect PVD and ALD Ru. In particular, the methyl precursors used for the CVD process lead to the incorporation of carbon impurities into the metal film, making the Ru bonds weaker by lowering the cohesive energy of the material [5]. The H₂ annealing performed after the deposition to remove the impurities is not sufficient for the 10 nm-thick Ru film. In addition, the CVD Ru film is extremely rough at the metal/dielectric interface because it does not nucleate uniformly on the not-fully closed TiN adhesion layer; the surface roughness might result in a local enhancement of the electric field. CVD Ru is thus more susceptible to ionization at the metal/dielectric interface and more likely to diffuse into the dielectric under an applied electric field compared to its ALD and PVD equivalents, for which the high cohesive energy of the Ru reticle is preserved. By optimizing the deposition recipe, the performances could be improved in order to obtain for CVD Ru the same performances of ALD and PVD Ru.

Established that metal drift occurs for all metal/oxide combinations, to confirm that metal drift is caused by the characteristics of our CVD Ru and not by the oxide thickness, TDDB at 100 °C and 200 °C were also performed on a 40 nm-thick PECVD SiO₂ and compared to the experimental data from [8] (see Fig. 4). In fact, one could expect a significant impact of the oxide thickness on metal-drift induced failure, not only for the different conduction mechanisms that characterize ultra-thin oxides [9]. First, according to the model proposed by Wu et al. [10] to describe metal drift induced failure in BEOL and MOL systems, the time needed for the metal filament to form strongly depends on barrier continuity (here the same for all samples) and oxide thickness. In

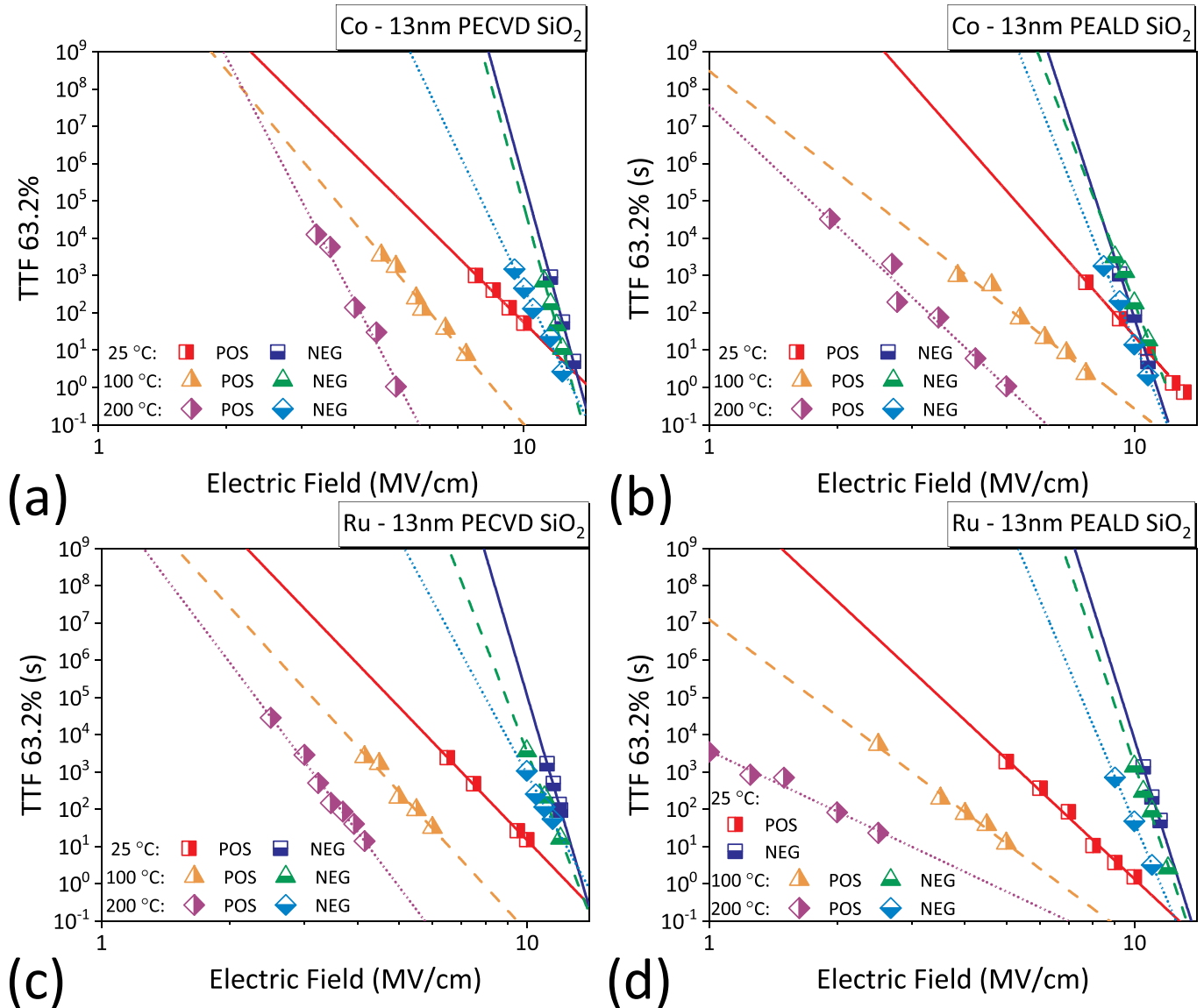


Fig. 3. TDDDB data gathered at 25 °C, 100 °C and 200 °C for p-caps with (a) Co/PECVD SiO₂, (b) Co/PEALD SiO₂, (c) Ru/PECVD SiO₂ and (d) Ru/PEALD SiO₂. The power-law model ($t_{tf63.2\%} \sim E^{-m}$) was used to fit the data. A clear increase in m at 200 °C is observable in (a).

addition, a higher defectivity could be expected in ultra-thin oxides grown at low temperatures, especially for PEALD oxide, that could affect both intrinsic and metal drift induced breakdown. Whereas the TDDDB data for negative stress voltages (intrinsic breakdown) do not depend on the Ru deposition technique and oxide thickness, metal drift is instead clearly visible for positive stress voltages only for CVD Ru. Consequently, we can conclude that metal-drift induced failure observed with our CVD Ru is caused by the recipe used to deposit the film and not by the oxide thickness.

2.4. Metal filament formation and growth model

In Fig. 5a and Fig. 5b the acceleration factors extracted from the various data sets are plotted.

As expected, negative acceleration factors are quite high ($m > 20$), especially at 25 °C. However, whereas for Ru m_{NEG} is approximately the same for PEALD and PECVD oxide, in the case of Co quite a large difference is visible when comparing the values for the two kinds of oxide as already observed for the k value (Table 1). Despite the large drop as the temperature is decreased, the negative acceleration factors remain high even at 200 °C.

On the other hand, positive acceleration factors are lower than the corresponding negative values, even at 25 °C, for both Co and Ru metallization schemes, indicating that both metals are significantly affected by metal drift. However, the plots in Fig. 5 clearly show an increase in the acceleration factor at 200 °C in all cases but for Co/PEALD SiO₂; the increase is particularly large in the case of Co/PECVD oxide for which m_{POS} almost doubles. Such an increase is characteristic of the

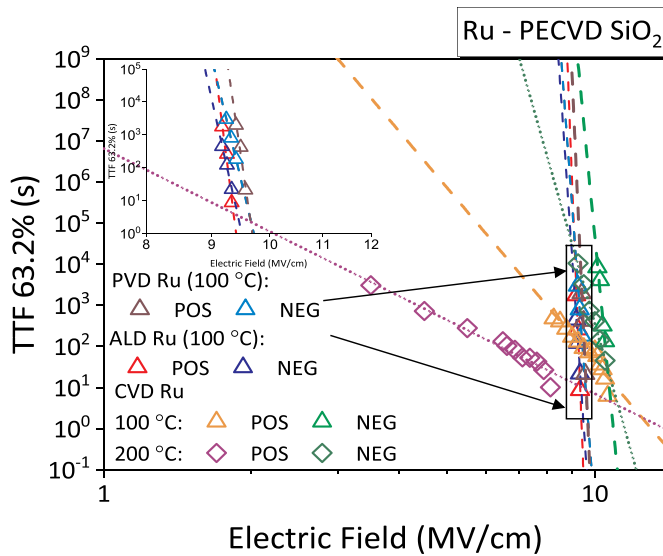


Fig. 4. TDDB data at 100 °C and 200 °C measured on p-caps with CVD Ru and 40 nm PECVD SiO₂ show that CVD Ru drift does not depend on oxide thickness. TDDB data from [8] (also in the inset) for ALD and PVD Ru are shown for comparison.

filament formation regime [10] since at low fields, as those used for TDDB measurements at 200 °C, the time required for a critical mass amount of metal ions to accumulate at the metal/dielectric interface and penetrate the dielectric could be very long.

Fig. 5c and Fig. 5d show the β value extracted from the Weibull distributions. The values for positive stress voltages are very low, supporting the conclusion that metal drift occurs in all the characterized metal/dielectric combinations. It is worth noticing that for the case of Co/PEALD SiO₂ β is quite low for both voltage polarities and all temperatures suggesting a particularly low quality of the oxide film that could also explain why no increase in acceleration factor was observed for this specific case.

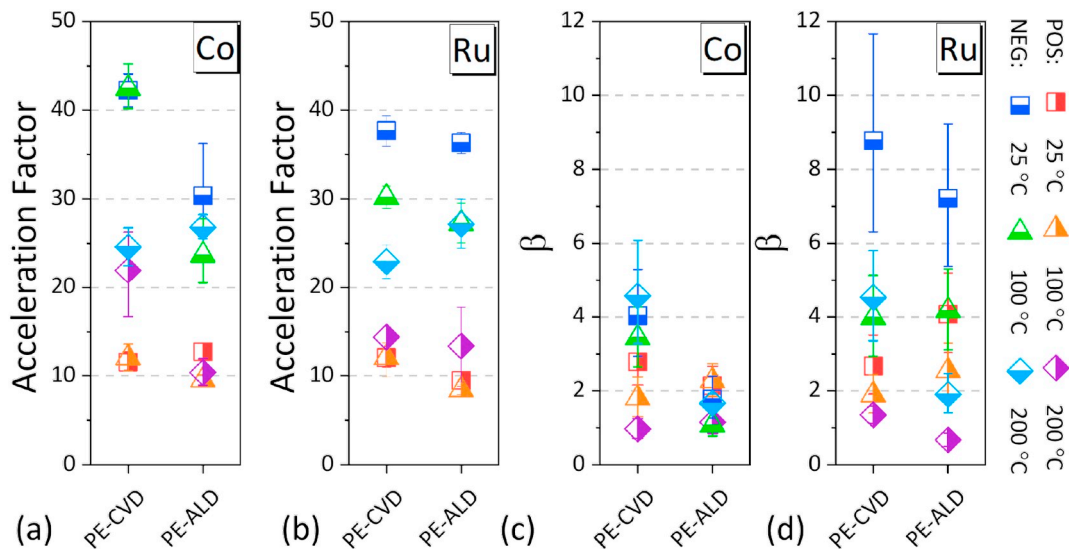


Fig. 5. Acceleration factor for (a) Co and (b) Ru p-caps extracted from TDDB data in Fig. 3. In (c) and (d) the β -slope of the Weibull distributions for Co and Ru, respectively.

2.5. The role of SiO₂

Overall, a difference in performance could be observed between PECVD and PEALD oxide films, with the latter exhibiting lower performances. Such a difference is particularly evident when metal drift occurs; with all other things being equal, Co and Ru are more likely to ionize when in contact with PEALD oxide. The difference can be explained by considering the deposition conditions of low temperature PEALD SiO₂ for which oxygen plasmas are used to promote the growth. Consequently, extra O₂ might be present at the top interface onto which the metal is deposited [14] thus favouring the ionization processes at the metal/dielectric interface. On the other hand, it has been reported in literature that metal drift is partially hindered by the positive charges that are usually present in PECVD oxide films; the positive charges repulse part of the metal ions, reducing the fraction entering the oxide to form the filament [12,13].

3. Conclusions

In this study we evaluated metal drift induced failure in ultra-thin oxides with Co and Ru metallization schemes, both deposited by CVD. In particular, we investigated the impact of oxide thickness and deposition technique as well as Ru deposition conditions on metal drift. We found that, differently to PVD and ALD Ru, CVD Ru is affected by metal drift. We concluded that carbon impurities are incorporated in the Ru film as a consequence of the precursors used in the CVD process. Carbon impurities lower the cohesive energy of Ru and compromise its resilience to metal drift. Furthermore, for both Co and Ru, the oxide thickness is not the determining factor for metal drift. In addition, consistently to what reported in literature, we also observed better performances with PECVD SiO₂ than with PEALD SiO₂ because of the positive charges present at metal/dielectric interface in the case of PECVD SiO₂ that hinder the migration of metal ions into the dielectric. Finally, experimental data confirmed the validity of the metal formation and growth filament model since we clearly observed an increase of the acceleration factors at low fields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the contributions from all members of the Advanced Interconnect Program.

References

- [1] K. Fuchs, The conductivity of thin metallic films according to the electron theory of metals, *Math. Proc. Camb. Philos. Soc.* 34 (1) (1938) 100–108.
- [2] E.H. Sondheimer, The influence of a transverse magnetic field on the conductivity of thin metallic films, *Phys. Rev.* 80 (3) (1950) 401–406.
- [3] R.H. Kim, B.H. Kim, T. Matsuda, J.N. Kim, J.M. Baek, J.J. Lee, J.O. Cha, J.H. Hwang, S.Y. Yoo, K.M. Chung, K.H. Park, Highly reliable Cu interconnect strategy for 10nm node logic technology and beyond, 2014 IEEE IEDM, IEEE, 2014, pp. 32-2–32-4.
- [4] Y.K. Siew, N. Jourdan, Y. Barbarin, J. Machillot, S. Demuynck, K. Croes, J. Tseng, H. Ai, J. Tang, M. Naik, P. Wang, CVD Mn-based self-formed barrier for advanced interconnect technology, 2013 IEEE IITC, 2013, pp. 1–3.
- [5] C. Adelman, L.G. Wen, A.P. Peter, Y.K. Siew, K. Croes, J. Swerts, M. Popovici, K. Sankaran, G. Pourtois, S. Van Elshocht, J. Bömmels, Alternative metals for advanced interconnects, 2014 IEEE IITC, 2014, pp. 173–176.
- [6] S. Dutta, S. Kundu, A. Gupta, G. Jamieson, J.F. Granados, J. Bömmels, C.J. Wilson, Z. Tőkei, C. Adelman, Highly scaled ruthenium interconnects, *IEEE Electron Device Lett* 38 (7) (2017) 949–951.
- [7] S. Dutta, S. Beyne, A. Gupta, S. Kundu, S. Van Elshocht, H. Bender, G. Jamieson, W. Vandervorst, J. Bömmels, C.J. Wilson, Z. Tőkei, Sub-100nm² Cobalt Interconnects, *IEEE Electron Device Lett* 39 (5) (2018) 731–734.
- [8] O.V. Pedreira, K. Croes, A. Leśniewska, C. Wu, M.H. Van Der Veen, J. de Messemaeker, K. Vandersmissen, N. Jourdan, L.G. Wen, C. Adelman, B. Briggs, Reliability study on cobalt and ruthenium as alternative metals for advanced interconnects, 2017 IEEE IRPS, 2017, pp. 6B–2.
- [9] E.Y. Wu, J. Suñé, R.P. Vollertsen, Comprehensive physics-based breakdown model for reliability assessment of oxides with thickness ranging from 1 nm up to 12 nm, 2009 IEEE IRPS, 2009, pp. 708–717.
- [10] C. Wu, O.V. Pedreira, A. Leśniewska, Y. Li, I. Ciofi, Z. Tőkei, K. Croes, Insights into metal drift induced failure in MOL and BEOL, 2018 IEEE IRPS, 2018, pp. 3A–1.
- [11] L. Zhao, M. Pantouvaki, K. Croes, Z. Tőkei, Y. Barbarin, C.J. Wilson, M.R. Baklanov, G.P. Beyer, C. Claeys, Role of copper in time dependent dielectric breakdown of porous organo-silicate glass low-k materials, *Appl. Phys. Lett.* 99 (22) (2011) 222110.
- [12] K. Hozawa, J. Yugami, Copper diffusion behaviour in SiO₂/Si structure during 400° C annealing, *Jpn. J. Appl. Phys.* 43 (1R) (2004) 1.
- [13] D.A. Buchanan, J.H. Stathis, P.R. Wagner, Trapped positive charge in plasma-enhanced chemical vapor deposited silicon dioxide films, *Appl. Phys. Lett.* 56 (11) (1990) 1037–1039.
- [14] L.J. Raaijmakers, Current and future applications of ALD in micro-electronics, *ECS Trans.* 41 (2) (2011) 3–17.
- [15] F. Chen, O. Bravo, K. Chanda, P. McLaughlin, T. Sullivan, J. Gill, J. Lloyd, R. Kontra, J. Aitken, A comprehensive study of low-k SiCOH TDDDB phenomena and its reliability lifetime model development, 2006 IEEE IRPS, 2006, pp. 46–53.
- [16] S.-C. Lee, A.S. Oates, K.-M. Chang, IEEE IRPS, 2009 (2019), p. 481.
- [17] S.Y. Jung, B.J. Kim, N.Y. Lee, B.M. Kim, S.J. Yeom, N.J. Kwak, Y.C. Joo, Bias polarity and frequency effects of Cu-induced dielectric breakdown in damascene Cu interconnects, *Microelectron. Eng.* 89 (2012) 58–61.
- [18] J. Suñé, E.Y. Wu, A new quantitative hydrogen-based model for ultra-thin oxide breakdown, 2001 Symposium on VLSI Technology, 2011, pp. 97–98.
- [19] J. Suñé, E.Y. Wu, Generalized hydrogen release-reaction model for the breakdown of modern gate dielectrics, *J. Appl. Phys.* 114 (1) (2013) 014–103.
- [20] E.Y. Wu, J. Suñé, Power-law voltage acceleration: a key element for ultra-thin gate oxide reliability, *Microelectron. Reliab.* 45 (12) (2005) 1809–1834.