Zirconium Dioxide Thin Films for Microelectronics Deposited by Metal Organic Chemical Vapor Deposition

S. Harasek, H.D. Wanzenböck, B. Basnar, J. Smoliner, and E. Bertagnolli

Institute for Solid State Electronics, Vienna University of Technology

The metal-organic chemical vapor deposition (MOCVD) of ultrathin zirconium dioxide from Zr(tfacac)$_4$ on (100) silicon is thoroughly investigated. Physical characterization addresses the evolution of surface topography and the impact of processing parameters on the chemical composition of the films to provide a sound basis for the discussion of electrical properties. Electrical investigation by means of MOS structures has been performed to assess the interface quality and the dielectric properties of the layers. Interface trap density is observed to be around 5.10^{11} cm^{-2}.eV^{-1} at midgap for (100)-oriented substrates. Leakage currents in the ultrathin regime are significantly reduced compared to equivalent SiO$_2$-layers. The temperatures throughout the gate insulator formation process do not need to exceed 650 °C, and thus allow keeping the thermal budget low.

Introduction

Currently the search for a suitable high permittivity dielectric for the forthcoming replacement of SiO$_2$ as gate dielectric in leading-edge complementary MOS (CMOS) devices provides enormous impetus in this field of materials science. Yet, the identification of a suitable material may only be considered a partial success, since besides the material's properties themselves the entity of material and deposition method must meet the requirements for compatibility with CMOS technology.

While the various methods based on physical vapor deposition (PVD) provide a convenient means for the evaluation of materials systems for alternate dielectric applications, technological considerations concerning device morphology in general rule out such line-of-sight PVD processes as stated by G.D. Wilk *et al.* [1]. On the other hand, different methods of chemical vapor deposition (CVD) have proven quite successful in providing uniform coverage over complicated device topologies. Therefore, our approach utilizes MOCVD, which in general allows processing at lower temperatures than CVD from inorganic precursors.

Group IVB oxides and materials based on these oxides are among the most promising candidates for the succession of SiO$_2$ as gate dielectric. This is mainly due to their dielectric constants around 20 and – maybe of even higher importance – the sufficient band-offsets provided towards silicon (as displayed in Fig. 1) to suppress tunneling.

We evaluate the properties of thin films of zirconium dioxide with equivalent oxide thicknesses (EOTs) down to the 2 nm range. Chemical composition, surface topography and electrical properties are examined in dependence on thin film processing.

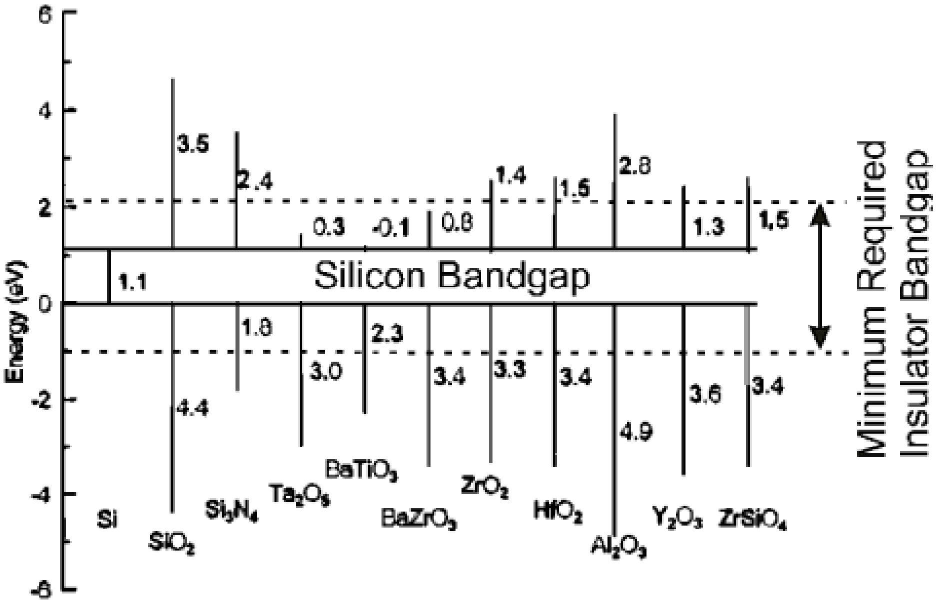

Fig. 1: Band-offsets in respect to silicon provided by several high-k materials. Minimum requirements are indicated (adapted from [2]).

Experimental

Thin films were deposited on p-type silicon (100). The deposition apparatus consisted of a horizontal hot wall reactor with a bubbler system for the delivery of the metal-organic precursor substance. Zirconiumtetrakistrifluoroacetylacetonate was used as precursor due to the favorable properties of this substance in terms of stability and volatility. A detailed description of the deposition process is given in [3]. In order to improve thin film properties different annealing procedures were tested. Oxidizing (20% oxygen in nitrogen) as well as reducing (forming gas, 10% hydrogen in nitrogen) atmospheres were used during annealing at 650 °C. The chemical composition of the films was analyzed by Auger electron spectroscopy (AES) before and after annealing. Surface topography of the deposited films was examined by atomic force microscopy (AFM). For the evaluation of the electrical properties of the thin films, MOS capacitors were constructed. Capacitance-voltage (C-V) and current-voltage (I-V) measurements provided information about EOT, trap and charge densities as well as leakage currents.

Results and Discussion

Topography of the deposited films was evaluated by AFM. The relative roughness ($R_{a, rel}$) as the ratio of absolute roughness R_a and total film thickness was used for comparison of the results. This evaluation shows a deposition at 450 °C to result in minimum surface roughness. The graph on the left in Fig. 2 presents the evolution of the relative surface roughness for films with thicknesses up to about 400 nm. The AFM surface plot to the right of Fig. 2 shows that for very low film thicknesses much smoother films – on absolute and relative scale – are obtained. The roughness of the 15 nm thick film amounts to only R_a = 0.135 nm, equaling less than 1 % relative roughness.

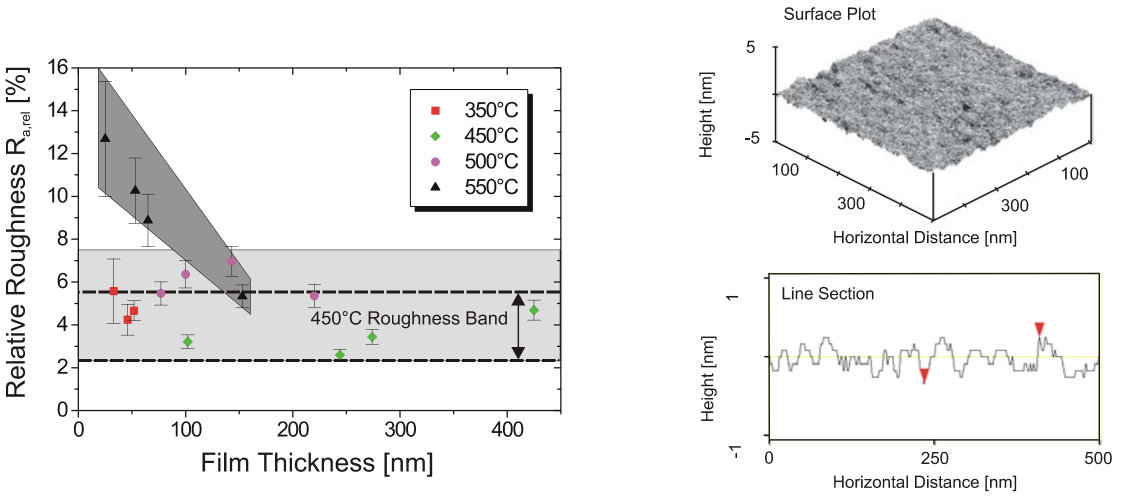

Fig. 2: Left: The evolution of surface roughness with film thickness for thicknesses up to 400 nm. 450 °C deposition temperature leads to smoothest films. Right: AFM surface plot of a 15 nm ZrO_2 thin film deposited at 450 °C. A surface roughness of $R_a = 0.135$ nm is observed with a peak-to-peak roughness of 0.58 nm in the displayed line section.

This improvement of the film smoothness in the ultrathin film region may be connected to a change in the crystallinity of the films. While transmission electron microscopy (TEM) showed thicker films to be polycrystalline, the smoother surface of the thinnest films possibly points to an amorphous state of these films. However, definitive results are not available by now, and the issue deserves closer attention and clarification by high-resolution TEM examination.

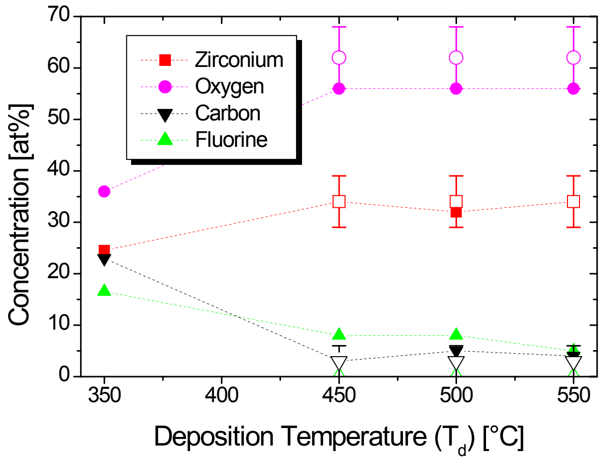

Fig. 3: Chemical composition of thin films deposited at various temperatures (full symbols) and composition achieved after post-deposition annealing (open symbols). For reasons of clarity, the estimated error is indicated for the composition after annealing only.

Figure 3 shows the chemical composition of the films in dependence on the deposition temperature. The unfavorable effect of a too low deposition temperature is clearly discernable, while for medium temperatures a constant film composition is observed only suffering a slight oxygen deficiency. After annealing in either diluted oxygen or forming gas at temperatures of 650 °C or above, the film composition closely approaches the stoichiometric composition ZrO_2. After temperature treatment, the remaining carbon impurities are at a negligible level at the limit of detection.

Al-ZrO_2-p$^+$Si capacitor structures served as test vehicles for the evaluation of the electrical characteristics of the processed thin films. EOTs down to the 2 nm range have been realized sustaining favorable dielectric and interface properties. Figure 4 displays on the left the C-V curve of a MOSCAP featuring a dielectric with 2 nm EOT of zirconium dioxide as obtained after annealing in diluted oxygen. A flatband voltage shift (ΔV_{FB}) of about –600 mV and minor distortion near midgap is observed in a generally well-behaved curve. The C-V plot on the right side shows that ΔV_{FB} as well as the distortion near midgap are minimized if forming gas is used as annealing atmosphere. However, in this case only EOTs down to about 3 nm are accessible, while post-deposition annealing in an oxidizing atmosphere was found to further reduce EOT.

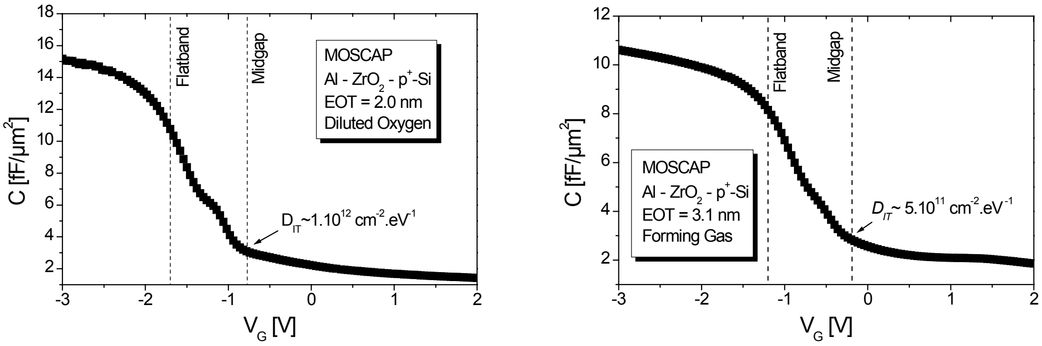

Fig. 4: C-V curves of MOSCAPs with ZrO_2 dielectrics annealed either in diluted oxygen (left) or forming gas (right). Lower EOTs are observed after annealing in oxygen, while electrical characteristics are more favorable after annealing in forming gas.

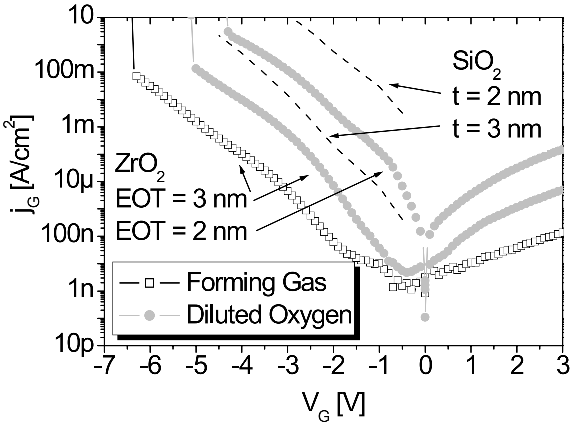

Fig. 5: I-V properties of Al-ZrO_2-p$^+$Si MOSCAPs. A more than three decades lower leakage than in SiO_2 is observed for ZrO_2 after annealing in forming gas. SiO_2 leakage characteristics are extracted from [4], [5].

Using Terman’s method, interface trap densities (D_{IT}) of differently annealed samples were computed. For samples annealed in forming gas, D_{IT} values around 5.10^{11} $cm^{-2}.eV^{-1}$ are usually obtained. Comparable samples annealed in diluted oxygen displayed a higher D_{IT} in all cases. The I-V properties of the thin films are depicted in Fig. 5. For both kinds of anneal ZrO_2 provides a significant decrease in gate leakage compared to SiO_2. A reduction of leakage by more than a factor of 10^3 can be accomplished for 3 nm EOT. Again a forming gas anneal proves advantageous for optimization of the material’s performance, suggesting the formation of a large amount of additional charges and traps during annealing in the oxidizing atmosphere. Overall, the impact of the annealing atmosphere on the electrical properties of the films is much stronger than expected from compositional analysis.

Conclusion

The formation of high-quality ZrO_2 thin films on silicon by MOCVD has been successfully demonstrated. Compositional as well as electrical characterization unveils promising properties of the thin films down to the 2 nm EOT range. Throughout the gate insulator formation, processing temperatures do not require to exceed 650 °C, keeping the thermal budget low. Owing to these circumstances, further research to establish film deposition from metal-organic precursor substances in silicon technology is encouraged.

Acknowledgements

The authors would like to thank Josef Brenner and Prof. Herbert Stoeri of the “Institut für Allgemeine Physik” for Auger analysis.

References

[1] G.D. Wilk, R.M. Wallace, J.M. Anthony: *J. Appl. Phys.* **89**, 5243 (2001).

[2] J. Robertson: *J. Vac. Sci. Technol. B* **18 (3)**, 1785 (2000).

[3] S. Harasek, H.D. Wanzenboeck, B. Basnar, J. Smoliner, J. Brenner, H. Stoeri, E. Gornik, and E. Bertagnolli: *Thin Solid Films* **414**, 199 (2002).

[4] K. F. Schuegraf and C. Hu: *Semicond. Sci. Technol.* **9**, 989 (1994).

[5] B. Brar, G. D. Wilk, and A. C. Seabaugh: *Appl. Phys. Lett.* **69**, 2728 (1996).