HAFNIUM TITANIUM SILICATE HIGH-k DIELECTRIC FILMS DEPOSITED BY MOCVD USING NOVEL SINGLE SOURCE PRECURSORS

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Future technologies for the manufacturing of field effect transistors (FETs) with dimensions of less than 100 nm require a replacement of silicon dioxide as the dielectric material. Otherwise, leakage currents in the transistors become too big due to a required film thickness of less than 1 nm (1). The new material has to meet several specifications:

1. a dielectric constant higher than 20 compared to SiO_2 of 3.9;
2. thermal stability up to 900 °C;
3. no reaction with elemental silicon which could form a low k interface layer, and
4. low leakage currents.

The Group IV metal oxides ZrO_2 and HfO_2 respectively their silicates are good candidates to fulfill these requirements (2-13). Thermal stability issues found in the case of zirconium changed the focus to the hafnium-based materials (14). SiO_2 is introduced into these materials to increase the crystallization temperature and therefore the thermal stability. A second positive effect of adding SiO_2 is the reduced oxygen conductivity of the films. This oxygen conductivity of ZrO_2 and HfO_2 films is believed to be the main reason for the formation of SiO_2 respectively silicate interface layers between the substrate and the films (15-16). The main disadvantage of adding SiO_2 is the decrease of the dielectric constant compared to pure ZrO_2 and HfO_2.

In contrast to HfO_2 and ZrO_2, TiO_2 is lacking the thermodynamic stability on silicon and has a lower band gap. On the other hand, the higher dielectric constant of titanium dioxide could be advantageous (k TiO_2 = 56 to 85; k HfO_2 = 25 to 40) (2-5, 17).

A promising idea is therefore to dope hafnium silicate with titanium oxide to increase the permittivity of the new material while keeping the good thermal stability. $Zr_xTi_yO_z$ deposited by atomic layer deposition has been studied before (18) but no publications about $Hf_xTi_ySi_zO_q$ have been presented to the best of our knowledge.

We present here an MOCVD approach for the deposition of such films, using two isostructural single source precursors, one containing hafnium and silicon and another one containing titanium and silicon. The precursors used are isostructural to the previously published single source zirconium silicate precursors recently developed in our group (10, 19-20). In distinction to the earlier studies, a liquid injection process is used in order to be able to easily adjust the ratio of the two precursors. The deposition behavior and the composition of the films was studied, as well as their optical properties.

1.Semiconductor Industry Association International, International Technology Roadmap for Semiconductors, http://public.itrs.net/ (2000)
2.The Physics and Chemistry of SiO_2 and the Si-SiO_2 Interface/495, H. Z. Massoud, I. J. R. Baumvol, M. Hirose, E. H. Poindexter, Editors, Vol. 2000-2,The Electrochemical Society, Inc., Toronto, Canada (2000)
3.Ultrathin SiO_2 and High-K Materials for ULSI Gate Dielectrics, H. R. Huff, C. A. Richter, M. L. Green, G. Lucovsky, T. Hattori, Editors, Vol. 567, Material Research Society Symposium Proceedings, Warrendale, PA (1999)
4.Chemical Processing of Dielectrics, Insulators and Electronic Ceramics, A. C. Jones, J. Veteran, D. Mullin, R. Cooper, S. Kaushal, Editors, Vol. 606, Material Research Society Symposium Proceedings, Warrendale, PA (1999)
5.R. M. Wallace, G. D. Wilk, Semicond. Int. **24**, 227 (2001)
6.G. D. Wilk, R. M. Wallace, J. M. Anthony, J. Appl. Phys, **87**, 484 (2000)
7.R. G. Gordon, J. Becker, D. Hausmann, S. Suh, Chem. Mater., **13**, 2463 (2001)
8.R. Therrien, B. Rayner, G. Lucovsky, in The Physics and Chemistry of SiO_2 and the Si-SiO_2 Interface/495, H. Z. Massoud, I. J. R. Baumvol, M. Hirose, E. H. Poindexter, Editors, Vol. **2000-2**,The Electrochemical Society, Inc., Toronto, Canada (2000)
9.D. A. Neumayer, E. Cartier, J. Appl. Phys., **90**, 1801 (2001)
10.S. Zürcher, M. Morstein, N. D. Spencer, M. Lemberger, A. Bauer, Chem. Vap. Deposition, **8**, 171 (2002)
11.K. Kukli, M. Ritala, T. Sajavaara, J. Keinonen, M. Leskelä, Chem. Vap. Deposition, **8**, 199 (2002)
12.P. A. Williams, J. L. Roberts, A. C. Jones, P. R. Chalker, N. L. Tobin, J. F. Bickley, H. O. Davies, L. M. Smith, T. J. Leedham, Chem. Vap. Deposition, **8**, 163 (2002)
13.J. P. Chang, Y-S. Lin, K. Chu, J. Vac. Sci. Technol. B, **19**, 1782 (2001)
14.Future Gate Stack, Annual Report of International SEMATECH, www.sematech.org (2001)
15.K. J. Hubbard, D. G. Schlom, J. Mater. Res., **11**, 2757 (1996)
16.A. Kumar, D. Rajdev, D. L. Douglas, J. Am. Chem. Soc., **55**, 439 (1972)
17.J. Robertson, MRS Bulletin, **27**, 217 (2002)
18.A. Rahtu, M. Ritala, M. Leskelä, Chem. Mater., **13**, 1528 (2001)
19.M. Morstein, I. Pozsgai, N. D. Spencer, Chem. Vap. Deposition, **5**, 151 (1999)
20.M. Morstein, Inorg. Chem., **38**, 125 (1999)