Journal of ELECTRICAL ENGINEERING, VOL. 62, NO. 1, 2011, 54–56

COMMUNICATIONS

GADOLINIUM SCANDATE: NEXT CANDIDATE FOR ALTERNATIVE GATE DIELECTRIC IN CMOS TECHNOLOGY?

Karol Fröhlich * — **Ján Fedor** * — **Ivan Kostič** **
— **Ján Maňka** *** — **Peter Ballo** ****

The films of $GdScO_3$ were prepared by liquid injection metal-organic chemical vapor deposition, MOCVD at 600 °C on (100) Si substrate. The as-deposited films were amorphous with a smooth surface and sharp $GdScO_3$/Si interface. X-ray diffraction showed that the amorphous phase is well preserved upon rapid thermal annealing up to 1000 °C. It is shown, that exact stoichiometry of $GdScO_3$ is not necessary to achieve dielectric constant above 20.

Keywords: CMOS technology, gate dielectric, high-κ, X-ray diffraction, X-ray reflectivity

1 INTROUCTION

$GdScO_3$ thin films attracted recently attention as promising candidate for next generation of high-κ dielectrics in CMOS technology. Hf-based dielectrics, that are currently implemented in a production, suffer either from low recrystallization temperature ($\sim$ 500 °C for pure HfO_2) or from lowering of dielectric constant when introducing Si to enhance amorphous phase stability ($\kappa \sim 14 \div 16$ for HfSiO, depending on Si content). It is desirable that gate dielectric retains its amorphous structure during transistor processing and remains stable upon source/drain activation step and/or post-metallization annealing in reduction atmosphere.

The $GdScO_3$ films were prepared by pulsed laser deposition, PLD [1], electron beam evaporation [2], atomic layer deposition, ALD [3, 4] and metal organic chemical vapor deposition, MOCVD [5]. The dielectric constant of the prepared gadolinium scandate films is higher than 20 and allows for effective scaling of the transistor. First evaluation of thermal stability of $GdScO_3$ films indicated that the films remain amorphous even after 1000 °C annealing [1, 2]. However, before introducing the $GdScO_3$ thin films into CMOS technology, their properties should be thoroughly analysed and advantages over HfO_2 based dielectrics clearly identified.

In our contribution we present properties of $GdScO_3$ films prepared by liquid injection metal organic chemical vapor deposition. We describe dielectric properties and stability of the amorphous phase against recrystallization. Finally, appropriatness of $GdScO_3$ films as a next candidate for alternative gate dielectric is discussed.

2 EXPERIMENTAL METHODS

The $GdScO_3$ films were deposited at 600 °C in a low-pressure hot-wall quartz reactor. The solution of $Gd(thd)_3$ and $Sc(thd)_3$ precursors dissolved in toluene in a concentration of 0.02 M was introduced using computer controlled microvalve into the evaporation part heated at 250 °C. Opening time of the micro valve was 3 ms, resulting in the droplet mass of 5.7 mg. The reaction atmosphere was composed of O_2 (170 sccm flow) and Ar (21 sccm flow) with a total pressure of 200 Pa. Injection frequency was 0.33 Hz. Employing these parameters the film growth rate was adjusted to 0.8 nm/min. Si (100) oriented wafer slices were used as substrates. The substrates were cleaned in acetone, isopropyl alcohol and dipped in buffered HF before the deposition.

Composition of the films was varied by changing ratio of $Gd(thd)_3/Sc(thd)_3$ in a solution and verified by Rutherford backscattering. Backscattering spectrometry measurements were performed using $^4He^+$ ions with energy $E = 1.22$ MeV. Phase composition of the films was determined by grazing incidence X-ray diffraction using incidence angle of 1 deg. Surface and $GdScO_3$/Si interface quality was probed by X-ray reflectivity. The X-ray reflectivity was used to extract the thickness of the film. Both measurements were performed on Bruker AXS–D8 DISCOVER diffractometer using Cu Kα radiation. The films thicknesses determined by X-ray reflectivity were in good agreement with those obtained by Rutherford backscattering.

Dielectric constant of the $GdScO_3$ films was determined from capacitance- voltage measurements performed at the frequency of 1 MHz. For the capacitance-voltage measurement Ru films were deposited as gate electrodes by liquid injection MOCVD at 300 °C. The

---

Institute of Electrical Engineering, karol.frohlich@savba.sk ** Institute of Informatics, Institute of Measurement Science, *** Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava **** Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia

DOI: 10.2478/v10187-011-0009-z, ISSN 1335-3632

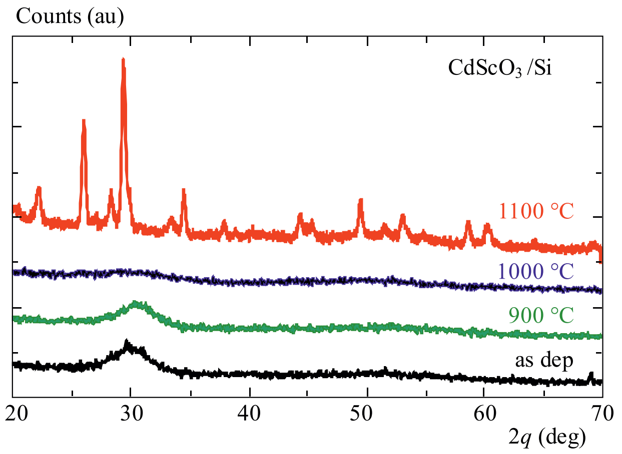

Fig. 1. Grazing X-ray diffraction patterns of the GdScO$_3$ films annealed at temperatures up to 1100 °C

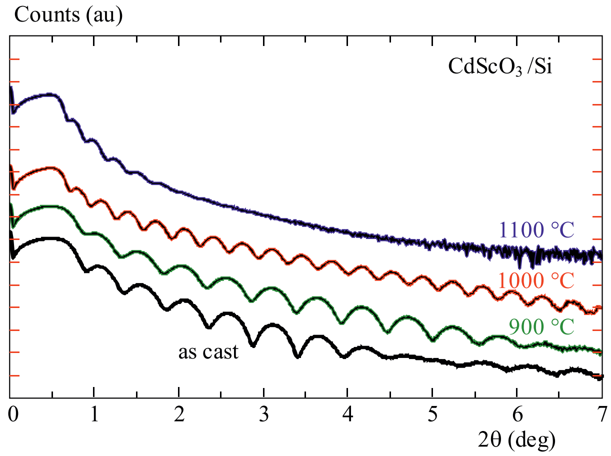

Fig. 2. X-ray reflectivity patterns of the GdScO$_3$ films annealed at temperatures up to 1100 °C

gate electrodes were patterned by standard optical lithography followed by Ar ion beam etching. The Al ohmic contacts on the back side of the Si substrate were prepared by vacuum evaporation using ATC Orion 8E (AJA Int.)

Thermal stability of the GdScO$_3$ films was examined by rapid thermal annealing (RTA) in N$_2$ atmosphere. The samples were heated using a ramp rate of 100 °C/s up to 900, 1000, and 1100 °C with a dwell time of 10 s.

3 RESULTS AND DISCUSSION

The as-deposited films exhibited amorphous character. Typical X-ray diffraction pattern of the as-deposited film is shown in Fig. 1. Wide maximum at 2 theta$\approx$ 30 deg indicates certain degree of short distance order of atoms along 111 planes. X-ray reflectivity pattern, Fig. 2, of as-deposited GdScO$_3$ films revealed oscillations up to $\sim$ 7 deg, indicating very smooth surface of the film and sharp GdScO$_3$/Si interface.

Crystallization of the films upon rapid thermal annealing was detected by X-ray diffraction and X-ray reflectivity. Figure 1 shows, that while after annealing at 900 °C the X-ray pattern remains unchanged. Enhanced modulation of the X-ray reflectivity pattern, Fig. 2, of the film annealed at 900 °C indicates improved smoothness of the surface and sharper interface. However, after 1000 °C processing the wide maximum in the X-ray diffraction pattern at $\approx$ 30 deg disappeared. Shorter period of the X-ray reflectivity modulation after annealing at 1000 °C suggests increasing of the film thickness. Analysis of the film annealed at 1000 °C by secondary ion mass spectroscopy (SIMS) revealed enhanced Si diffusion from the substrate through the whole GdScO$_3$ film [6]. Disappearance of the wide X-ray diffraction peak at $\approx$ 30 deg suggests thus amorphization of the film due to GdSc silicate formation. Similar effect was observed for 1000 °C annealed DyScO$_3$ film on Si substrate [7]. Recrystallization of the GdScO$_3$ film after rapid thermal annealing at 1100 °C is accompanied by suppression of the X-ray reflectivity modulation, indicating surface coarsening and GdScO$_3$/Si interface deterioration. Dielectric constant of oxide layer in metal-oxide-semiconductor structure was determined from the set of samples with various oxide thicknesses. Equivalent oxide thickness (*EOT*) of the metal-oxide-semiconductor can be expressed as

$$EOT = \frac{\kappa_{\mathrm{SiO_2}}}{\kappa_{\mathrm{ox}}} t_{\mathrm{ox}} + t_{\mathrm{SiO_2}} \tag{1}$$

where κ and t are dielectric constants and thicknesses of SiO$_2$ and oxide films, respectively. Plotting the *EOT* versus the t_{ox} we can determine dielectric constant κ_{ox} as well as physical thickness of the SiO$_2$ interfacial layer $t_{\mathrm{SiO_2}}$. Capacitance-voltage characteristics for set of GdScO$_3$ films with thickness ranged from 7.6 to 22.7 nm are shown in Fig. 3. Dielectric constant of 22 was extracted using equation (1), Fig. 4. The dielectric constant is comparable to those obtained by PLD [1] or ALD [3, 4] techniques. However, interface layer equal to $\sim$ 3 nm is relatively high. We suppose that the interface layer is formed during high deposition temperature (600 °C) of the GdScO$_3$ film.

We have examined dielectric properties of the GdScO$_3$ films with various cation composition Gd/(Gd+Sc). The composition was determined by Rutherford backscattering. For the composition range from 50 to 73 % Gd/(Gd+Sc) we observed nearly the same value value of the capacitance in accumulation. If we assume the same interface thickness for the films with various composition, the constant value of the capacitance in accumulation indicates independence of the dielectric constant on the composition. We believe, that this is due to amorphous character of the film. Consequently, exact stoichiometry of GdScO$_3$ is not necessary to achieve dielectric constant above 20. Similar weak dependence of dielectric constant on cation composition was observed for DyScO$_3$ in reference [8].

4 CONCLUSION

In conclusion, we have shown that thin GdScO$_3$ films with very smooth surface can be grown using liquid injection MOCVD. The films remain amorphous under rapid

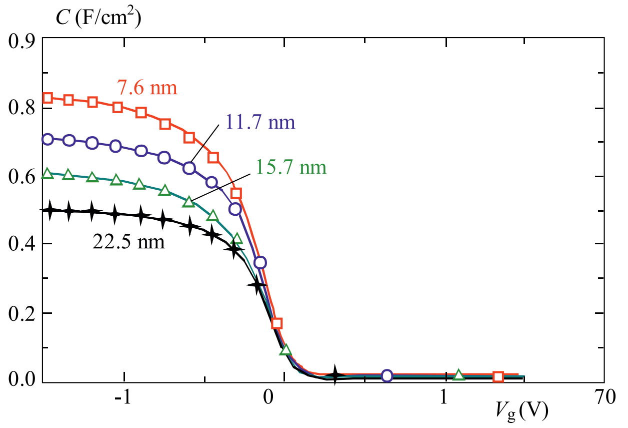

Fig. 3. Capacitance-voltage characteristics of the $GdScO_3$ films with various thickness

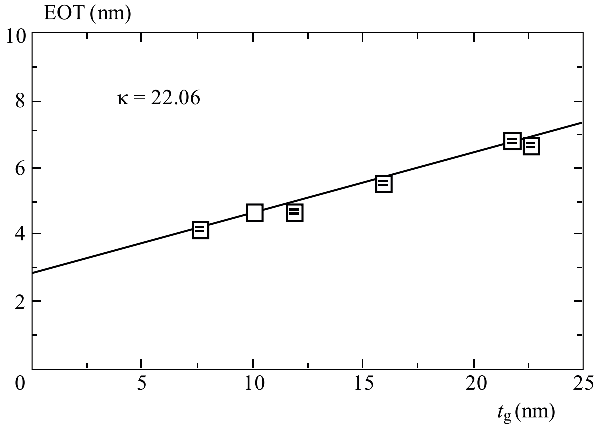

Fig. 4. Determination of dielectric konstant κ

thermal annealing up to 1000 °C. However, shorter modulation of the X-ray reflectivity pattern at 1000 °C indicates increase of the film thickness. As revealed by SIMS analysis, the increase of the film thickness is accompanied by intensive Si diffusion into the $GdScO_3$ layer, resulting in a formation of amorphous GdSc silicate. Consequently, amorphous structure of $GdScO_3$ films is less stable as it appears from the X-ray diffraction analysis alone. The amorphous structure of the films annealed at 1000 °C is preserved due to silicate phase formation.

Examination of dielectric properties of thin $GdScO_3$ films reveals that $GdScO_3$ can be considered for application as alternative gate dielectric in CMOS technology. The films can be prepared by deposition techniques already adopted in the silicon technology such as ALD or MOCVD. The films are amorphous and stable at temperatures up to 900 °C. Dielectric constant of thin $GdScO_3$ films is more than 20 and close to the composition 50 % Gd/(Gd+Sc) is nearly independent on the cation composition.

Acknowledgments

This work was supported by the Agency of the Ministry of Education, Science, Research and Sport for the EU structural funds for the support of R&D of science in the frame of the activity 2.1 Accessories for laboratory 1 – equipment for metal coating, project Centre of Excellence for New Technologies in Electrical Engineering, ITMS code 26240120011.

REFERENCES

[1] ZHAO, C.—WITTERS, T.—BRIJS, B.—BENDER, H.—RICHARD, O.—CAYMAX, M.—HEEG, T—SCHUBERT, J.—AFANASEV, V. V.—STESMANS, A.—SCHLOM, D. : Ternary Rare-Earth Metal Oxide High-κ Layers on Silicon Dioxide, Appl. Phys. Lett **86** (2005), 132903.

[2] WAGNER, M.—HEEG, T.—SCHUBERT, J.—LENK, S. T.—MANTL, S.—ZHAO, C.—CAYMAX, M.—DE GENDT, S. : Gadolinium Scandate Thin Films as an Alternative Gate Dielectric Prepared by Electron Beam Evaporation, Appl. Phys. Lett. **88** (2006), 172901.

[3] KIM, K. H.—FARMER, D. B.—LEHN, J. S. M.—RAO, P. V.—GORDON, R. G. : Atomic Layer Deposition of Gadolinium Scandate Films with High Dielectric Constant and Low Leakage Current, Appl. Phys. Lett. **89** (2006), 133512.

[4] MYLLYMÄKI, P.—ROECKERATH, M.—PUTKONEN, M.—LENK, S.—SCHUBERT, J.—NIINISTÖ, L.—MANTL, S. : Characterization and Electrical Properties of High-κ GdScO3 thin films grown by atomic layer deposition, Apl. Phys. A **88** (2007), 633–637.

[5] VINCZE, A.—LUPTÁK, R.—HUŠEKOVÁ, K.—DOBROČKA, E.—FRÖHLICH, K. : Thermal Stability of GdScO3 and LaLuO3 Films Prepared by Liquid Injection MOCVD, Vacuum **84** No. 1 (2010), 170–173.

[6] FRÖHLICH, K.—VINCZE, A.—DOBROČKA, E.—HUŠEKOVÁ, K.—ČIČO, K.—UHEREK, F.—LUPTÁK, R.—ŤAPAJNA, M.—MACHAJDÍK, D. : Thermal Stability of GdScO3 Dielectric Films Grown on Si and InAlN/GaN Substrates in CMOS Gate-Stack Scaling — Materials, Interfaces, and Reliability Implication, Mater. Res. Soc. Symp. Proc. **1155** (2009), C09–03.

[7] ADELMANN, C.—VAN ELSHOCHT, S.—FRANQUET, A.—CONARD, T.—RICHARD, O.—BENDER, H.—LEHNEN, P.—DE GENDT, S. : Thermal Stability of Dysprosium Scandate Thin Films, Appl. Phys. Lett. **92** (2008), 112902.

[8] THOMAS, R.—EHRART, P.—ROECKERATH, M.—VAN ELSHOCHT, S.—RIJE, E.—LUYSBERG, M.—BOESE, M.—SCHUBERT, J.—CAYMAX, M.—WASER, R. : Liquid Injection MOCVD of Dysprosium Scandate Films: Deposition Characteristics and High-κ Applications, J. Electrochem. Soc. **154** (2007), G147–G154.

Received 14 May 2010

Karol Fröhlich (Ing, DrSc) is a senior scientist at the Institute of Electrical Engineering, Slovak Academy of Sciences. He has finished his studies at the Faculty of Electrical Engineering, Slovak Technical University in 1976, received PhD degree in material science in 1988, DrSc degree In in 2001. His research activities include preparation and characterization of thin oxide films and their application in microelectronic devices. He has published over 90 scientific papers.

Ján Fedor, **Ivan Kostič**, **Ján Maňka** and **Peter Ballo**, for biographies see page 43 of this issue.