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Properties of thin films of high-*k* oxides grown by atomic layer deposition at low temperature for electronic applications

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Thin films of high-*k* oxides are presently used in semiconductor industry as gate dielectrics. In this work, we present the comparison of structural, morphological and electrical properties of binary and composite layers of high-*k* oxides that include hafnium dioxide (HfO_2), aluminum oxide (Al_2O_3) and zirconium dioxide (ZrO_2). We deposit thin films of high-*k* oxides using atomic layer deposition (ALD) and low growth temperature (60–240 °C). Optimal technological growth parameters were selected for the maximum smoothness, amorphous microstructure, low leakage current, high dielectric strength of dielectric thin films, required for gate applications. High quality of the layers is confirmed by their introduction to test electronic structures, such as thin film capacitors, transparent thin film capacitors and transparent thin film transistors. In the latter structure we use semiconductor layers of zinc oxide (ZnO) and insulating layers of high-*k* oxide grown by the ALD technique at low temperature (no more than 100 °C).

Keywords: high-*k* oxides, composite layers, atomic layer deposition, transparent electronics, zinc oxide.

1. Introduction

High-*k* oxide dielectrics are intensively tested as gate insulators for electronic applications, in particular for a next generation of thin films transparent electronic devices [1–9]. Properties of these materials such as a high dielectric constant and a wide band gap can result in desirable electrical characteristics, most of all, a low leakage current can be achieved [7, 8, 10]. The latter means that high-*k* oxides are considered as the alternatives to SiO_2 as a gate oxide in commercial electronic devices. For example, HfO_2 has already been used in 45 nm node processors [11]. The moti-

vation for this replacement was a too high gate current leakage due to a direct tunneling of electrons through a thin (about 1.4 nm) layer of SiO_2, exceeding 1 A/cm^2 at 1 V. In the consequence, a power dissipation has increased to unacceptable values [7, 8, 10]. Low standby power of the complementary metal oxide semiconductor (CMOS) requires a leakage current of below 1.5×10^{-2} A/cm^2 at 1 V, whereas for the dynamic random access memory (DRAM), a leakage current must be much smaller – 10^{-7} A/cm^2 at 1 V, rather than 1 A/cm^2 in structures with SiO_2 [7, 8, 12].

In this work we discuss properties of high-*k* oxides grown by the atomic layer deposition (ALD) method [13]. Deposition of these materials is the main application of ALD in the semiconductor industry from the time when the Intel Company used ALD for deposition of gate dielectrics in 45 nm, 32 nm, and recently 22 nm node generations of integrated circuits [11]. This method guarantees uniform coating of large substrates, reproducibility of deposition at the nanometre scale and low growth temperature. These properties make ALD an ideal technology for fabrication of various transparent dielectrics for semiconductors coating.

Transparent electronic materials are the most important candidates for a next generation of thin film applications (*e.g.*, as electronic paper – e-paper displays). Transparent thin film transistors based on wide band gap materials have been reported since 2003 [1, 3–5]. Wide band gap semiconductor oxides and insulating oxide materials were deposited on transparent substrates (foils, plastics, polymers, mylar, *etc*.) at low temperature to produce transparent devices for flexible, invisible and mechanically robust electronics [6]. The device processing temperature for these sensitive substrates is restricted to below 200 °C.

The development of insulating oxide materials for such electronic applications is more challenging than deposition of semiconductor layers. The quality of a gate insulator is highly critical, since it strongly affects a performance and stability of devices [1]. An optimal gate dielectric needs to accomplish the following important points: a relatively high dielectric constant and a wide band gap. The latter should be larger than that of the semiconductor materials to achieve a desirable conduction and valence band offsets of at least 1 eV [9], to avoid strong gate leakage and to provide a high dielectric strength. A good interface is also required, which can be easily achieved using amorphous dielectrics with a maximum smoothness of a surface [2, 9].

In this work, we compare structural, morphological and electrical properties of binary and composite layers of several high-*k* oxides, including hafnium dioxide (HfO_2), aluminum oxide (Al_2O_3) and zirconium dioxide (ZrO_2). The thin films of these high-*k* oxides are grown on various substrates and at low temperature (60–240 °C) using ALD.

2. Experiment

The thin films of high-*k* HfO_2, ZrO_2 and Al_2O_3 were used deposited on glass, quartz (SiO_2), *n*-type silicon (*n*-Si) and *p*-type gallium arsenide (*p*-GaAs) substrates by the ALD technique in a Savannah-100 reactor from Cambridge NanoTech Company.

Before the deposition, the substrates were cleaned in an ultrasonic bath with solvents (trichloroethylene, acetone and isopropanol) and deionized water. In the following deposition process we utilized the important advantage of the ALD method – process self-limitation and a sequential growth, which enable the use of very reactive precursors and in the consequence deposition at relatively low temperatures. In our approach we use tetrakis(dimethylamido)hafnium as a hafnium precursor, tetrakis(dimethylamido)zirconium as a zirconium precursor, trimethylaluminum as an aluminum precursor and deionized water as an oxygen precursor. The oxides were obtained at low temperature (often below 100 °C) by double-exchange chemical reactions:

$$Hf\left[(CH_3)_2N\right]_4 + 2H_2O \rightarrow HfO_2 + 4HN(CH_3)_2$$

$$Zr\left[(CH_3)_2N\right]_4 + 2H_2O \rightarrow ZrO_2 + 4HN(CH_3)_2$$

$$2Al(CH_3)_3 + 3H_2O \rightarrow Al_2O_3 + 6CH_4$$

In most of the ALD processes we limit the growth temperature to 100 °C, taking into account the possibility of deposition of thin films on conventional transparent and elastic substrates, as foils, which is required for production of emerging transparent electronic devices. The thickness of thin films scales with a number of the ALD cycles. Typical growth rates were about 0.14 nm for HfO_2, 0.09 nm for ZrO_2 and 0.10 nm per cycle for Al_2O_3. For organic precursors were short pulses of precursors of several milliseconds length.

The structural characterization of the so-obtained layers of high-*k* oxides was carried out by the X-ray diffraction (XRD) method using the X'Pert MPD diffractometer, equipped with an X-ray mirror and a two-bounce monochromator at the incident beam. The diffracted beam was measured with a 2-dimensional solid-state X-ray detector – PIXcel. The layers thickness was measured using the spectroscopic reflectometer Nanocalc 2000. The surface morphology was investigated by the atomic force microscopy (AFM, Bruker Dimension Icon) using the PeakForce Tapping and silicon nitride probes with sharp tips (a tip radius: 2 nm). The images of cross-sections were taken using the scanning electron microscopy (SEM, Hitachi SU-70) at 15 kV accelerating voltage. Optical transmission spectra were measured with the Solar CM2203 spectrometer. *I–V* electrical characterizations for metal–oxide–semiconductor (MOS) type structures were performed using Keithley 2601A and 2636A electrometers. In the latter case the capacitor-like structures (with the area of about 0.09 cm^2) were investigated deposited on semiconductor substrates – *n*-Si, *p*-GaAs and ZnO/SiO_2 (ZnO layers were grown by ALD at temperature of 100 °C). In these test structures a 10 nm Ti/40 nm Au gate electrode was evaporated using a photoresist mask, removed then by a lift-off process in solvents. Tests were performed on a series of MOS-type structures to check not only the devices performance, but also the uniformity of materials deposition.

3. Results and discussion

In this study we focus on the characteristics of binary and composite layers of selected high-*k* oxides – hafnium dioxide (HfO_2), zirconium dioxide (ZrO_2) and aluminum oxide (Al_2O_3). All of them are grown by ALD and optimized for electronic applications as insulators. Our aim is to select the optimal material/composite for the gate dielectric, with the optimized electrical parameters, but also with high transparency of an insulating material, and an atomically smooth surface. Oxide should have an amorphous structure and should provide a good interface with the upper semiconductor layer. The films should exhibit relatively high dielectric constants and a wide band gap to achieve a large breakdown field and a low leakage current, as required for practical applications [2].

In 2000 ROBERTSON reviewed candidates for gate oxides (such as Al_2O_3, ZrO_2, HfO_2, SrO, MgO, La_2O_3, TiO_2) [7–9]. He pointed out that values of dielectric constants vary inversely with band gap energies of these oxides. Thus, the optimal solution is the use of two or more dielectric materials, forming a multi-component combination of oxides, which should improve a device performance. Binary oxides with wider

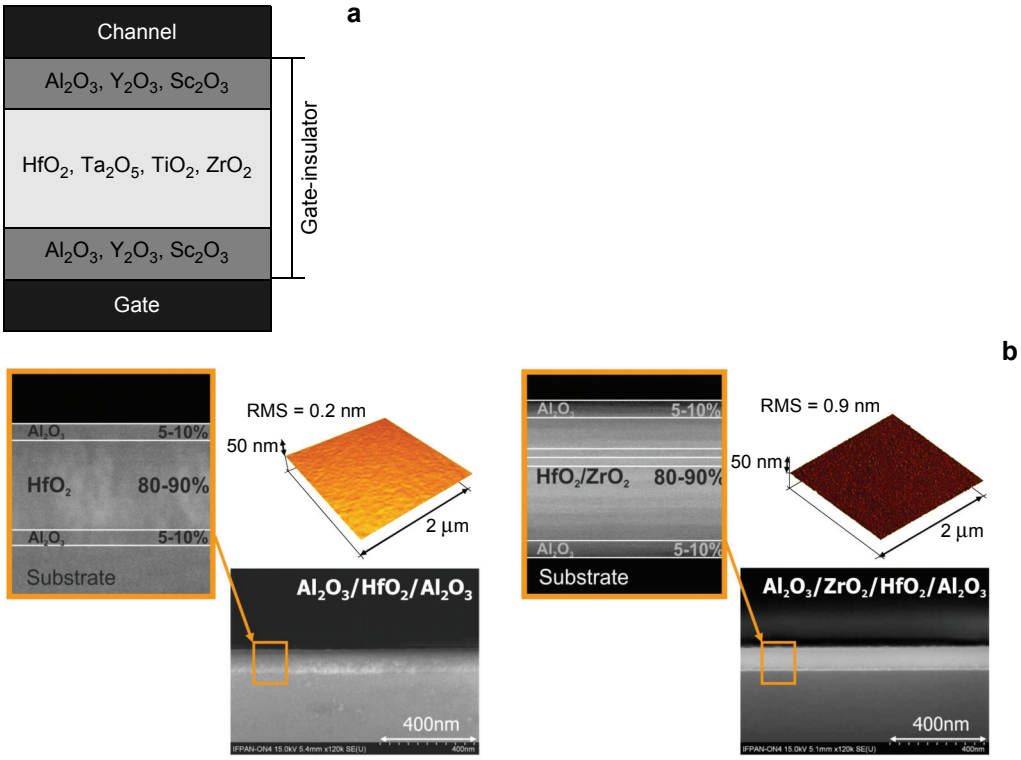

Fig. 1. Cross-sections of an optimal dielectric insulator for electronic applications (**a**, **b**). AFM images of surface morphology of composite layers of AHA and AZHA with thickness of 100 nm (**b**). Films were grown using the ALD method at temperature of 85 °C on a Si substrate.

band gaps (Al_2O_3, Y_2O_3, and perhaps Sc_2O_3) are attractive, since they allow to increase the breakdown voltage and thus to suppress the leakage current. In turn, other binary oxides (HfO_2, ZrO_2, Ta_2O_5, and TiO_2) have appreciably larger dielectric constants. Thus, these materials are also attractive as gate dielectrics, since their use allows the realization of strategy of the maximizing dielectric constant of the insulating layer.

Actually, the best solution which couples the advantages of both groups of dielectrics is introduction of composite structures, as illustrated in Fig. 1**a** [2]. Thus, the ALD technique was used to produce nanolaminate films of composite layers of $Al_2O_3/HfO_2/Al_2O_3$, labeled here as AHA (10 nm/80 nm/10 nm), and $Al_2O_3/ZrO_2/HfO_2/Al_2O_3$, labeled here as AZHA (10 nm/(5 nm/5 nm)×8/10 nm) (see Fig. 1**b**). In this way we produced films with a higher k value than alumina and a higher barrier than hafnia or zirconia. The thickness of these layers was 100 nm and the growth

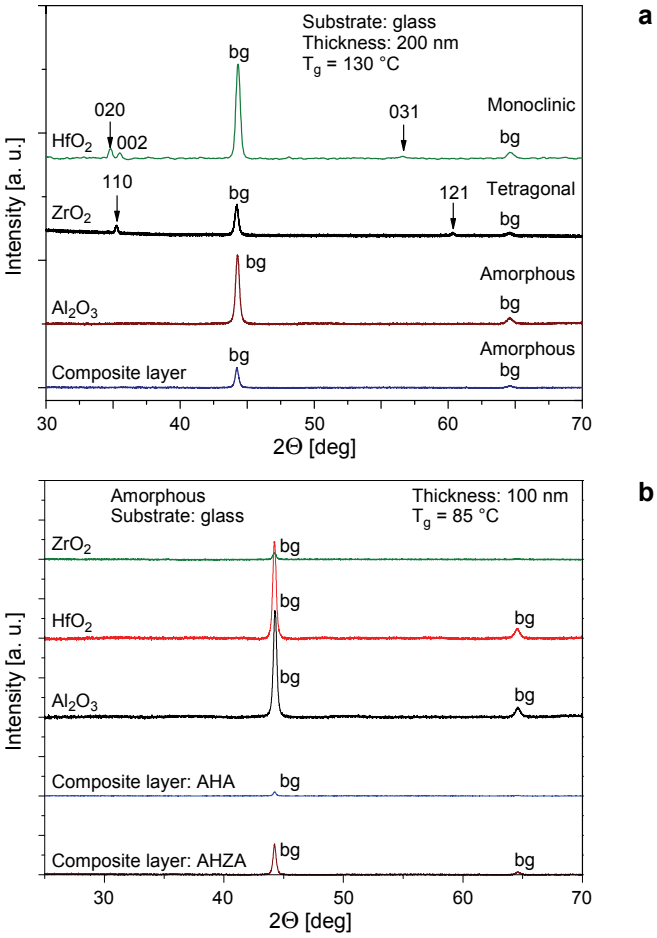

Fig. 2. The results of X-ray diffraction measurements of high-k oxide layers (**a**) with thickness of 200 nm at temperature of 130 °C (**b**) with thickness of 100 nm at temperature of 85 °C on a glass substrate obtained by ALD.

temperature was 85 °C. Hafnia, zirconia and alumina were selected for a gate insulator since they can be deposited as amorphous (as shown in Fig. 2**b**) binary and composite dielectric layers for layer thickness of 100 nm and a low growth temperature, below 100 °C.

Binary oxides such as HfO_2 and ZrO_2 often have a tendency to crystallize, even at low process temperatures [10]. This fact was already discussed in our recent publication [14]. We investigated the dependence of a crystallographic structure on a thickness and on a growth temperature of dielectric layers. We noted that films with a thickness of above 200 nm show a tendency to crystallize even at low growth temperature, see Fig. 2**a**. When thicker, HfO_2 layers crystallize in a monoclinic structure and ZrO_2 in a tetragonal structure. The trend to crystallize is a problem, since electrical parameters of the layers are affected by a layer crystallinity. It leads to rough interfaces and an appearance of grain boundaries, through which electrons can flow and ions can migrate. Therefore, the presence of grain boundaries between nanocrystallites decreases the reliability of electronic devices and increases a leakage current [10]. For these reasons we selected growth parameters and thickness of composite films and binary oxides to get consistently amorphous structures. Only such films show preferable electronic parameters. Moreover, amorphous films are also advantageous, because the smooth surfaces and the well-defined interfaces prevent the carrier flow from a semiconductor into an insulator, which reduces a leakage current density. Figures 1**b** and 2 confirm that the use of composite layers, such as AHA or AZHA, blocks crystallization of gate dielectrics. This ensures that amorphous layers with smoother surfaces are deposited.

The surface roughness of a gate insulator, determined by a root mean square (RMS) of the AFM measurements, should be kept as low as possible. The RMS roughness below 0.5 nm was achieved by us for oxide layers, including single materials such as

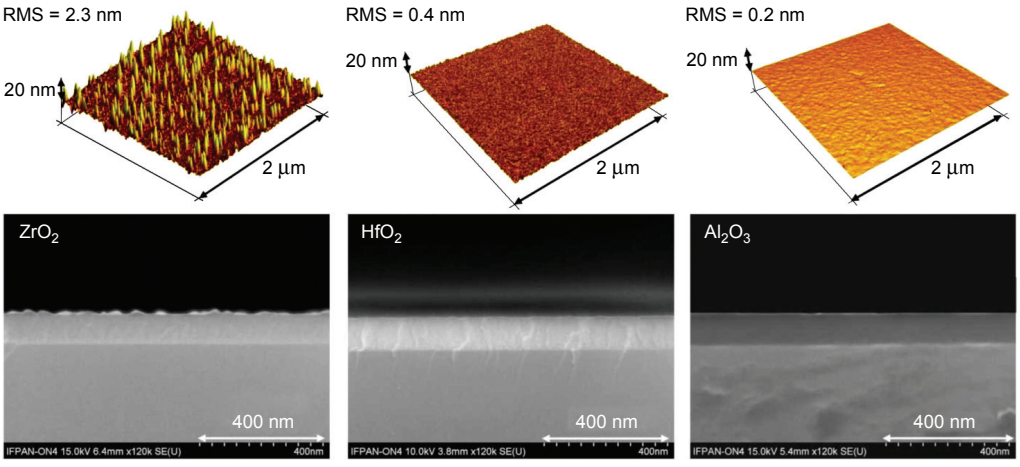

Fig. 3. AFM images of surface morphology and SEM cross-sections of ZrO_2, HfO_2 and Al_2O_3 layers with thickness of 100 nm. The structures were obtained by ALD at temperature of 85 °C on a Si substrate.

HfO_2 and Al_2O_3, as well as for composite layers – AHA (see Figs. 1**b** and 3). Figure 1**b** shows extremely low surface roughness, with the RMS value of 0.2 nm for these composite layers. Dielectric oxides with zirconia are characterized by a higher surface roughness, with the RMS values of above 2 nm for ZrO_2 layers and of below 1 nm for composite layers – AZHA (see Figs. 1**b** and 3). Films shown in Figs. 1**b** and 3 were grown at the same substrate temperature (85 °C) and have the same thickness of 100 nm. Film roughness scals with their thickness. Considering the roughness, the use of a composite dielectric structure was advantageous. We found that their surface roughness is lower than the roughness of single materials.

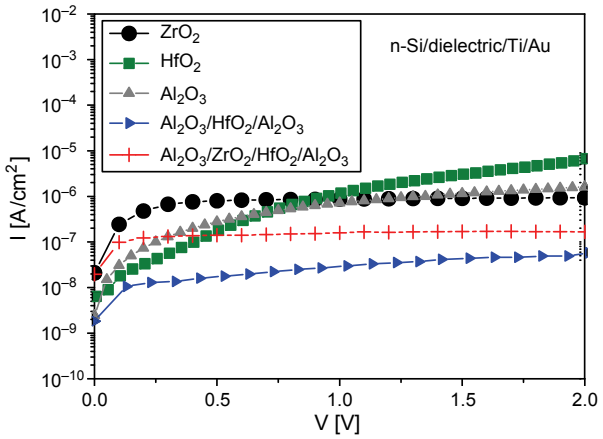

Fig. 4. *I–V* characterization of capacitor structures deposited on a silicon substrate with high-*k* oxide of 100 nm thickness grown by ALD at temperature of 85 °C.

Electrical characterization of dielectric layers shows that an optimal insulator consists of a composite layer of either AHA or AZHA (see Fig. 4 and Tab. 1). These structures are characterized by atomically smooth surfaces, an amorphous structure, a dielectric strength of about 4 MV/cm on a Si substrate and above 10 MV/cm for AHA on a transparent ZnO/SiO_2 substrate, a low leakage current below 5×10^{-8} A/cm^2 for AHA and below 5×10^{-7} A/cm^2 for AZHA on Si, as well as below 10^{-8} A/cm^2 for AHA on ZnO/SiO_2 substrate at 1 V, and by a relatively high dielectric constant of 19±3 (as compared to HfO_2 $k = 21\pm3$, ZrO_2 $k = 23\pm3$, Al_2O_3 $k = 10\pm3$). The resulting dielectric constants are favorably comparable with parameters reported in the literature

T a b l e 1. Electrical properties of capacitor structures grown by ALD on Si and GaAs substrates.

Dielectric layers [A/cm^2]	Dielectric constant k	Dielectric strength [MV/cm]	Leakage current at 1 V
HfO_2	21±3	< 1	~10^{-6}
ZrO_2	23±3	> 2	~10^{-6}
Al_2O_3	10±3	~ 1	~10^{-6}
Composite layers	19±3	> 4	~10^{-8}

[7, 8, 10, 15]. In practical applications, AHA was used as an insulating material, because AHA has a smoother surface and a lower leakage current than AZHA layers.

4. Conclusions

We demonstrate the deposition of high quality films of high-*k* dielectric oxides. The films are deposited at low temperature, below 100 °C. These insulators grown by the ALD method are promising materials due to their remarkable properties such as fine surface flatness, amorphous microstructure, high dielectric constant, low leakage current, high breakdown field, wide band gap sufficient to yield a band offset with respect to ZnO, and good uniformity. Furthermore, the investigated dielectrics exhibit high transparency, which exceeds 85% in the visible light range (see Fig. 5). Moreover,

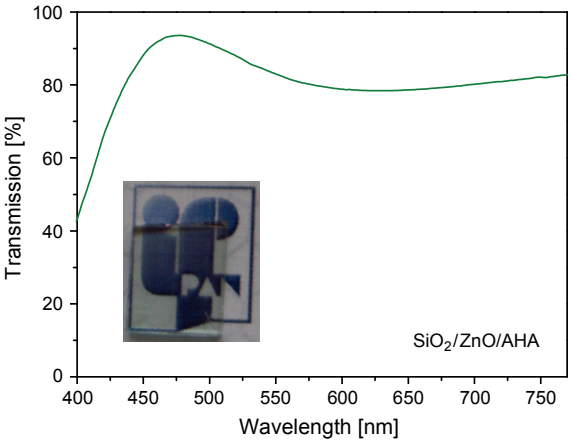

Fig. 5. Optical transmission spectrum of the quartz/ZnO/AHA structure. The inset shows a photograph of a 1 cm×1 cm glass substrate with the dielectric layer studied, placed on the text with the Institute of Physics logo, to demonstrate that our dielectric thin films are fully transparent to a visible light.

growth parameters are suitable for applications in transparent electronics. We show that the optimal solution for electronic applications is the use of two or more dielectric oxides, forming composite insulating layers. High quality of these layers is confirmed by investigations of test electronic structures, including transparent transistor structures. In the latter case we used as a semiconductor layer zinc oxide (ZnO) and composite dielectric layers of high-*k* oxides as a gate dielectric, all obtained by the ALD technique, as already reported in [16]. The combination of a low growth temperature and high transparency makes the ZnO-based transparent transistor structure with high-*k* dielectrics very promising for applications in transparent and flexible electronics.

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References

[1] WAGER J.F., *Transparent electronics*, Science **300**(5623), 2003, pp. 1245–1246.

[2] WAGER J.F., KESZLER D.A., PRESLEY R.E., *Transparent Electronics*, Springer, New York, 2008.

[3] MASUDA S., KITAMURA K., OKUMURA Y., MIYATAKE S., TABATA H., KAWAI T., *Transparent thin film transistors using ZnO as an active channel layer and their electrical properties*, Journal of Applied Physics **93**(3), 2003, pp. 1624–1630.

[4] HOFFMAN R.L., NORRIS B.J., WAGER J.F., *ZnO-based transparent thin-film transistors*, Applied Physics Letters **82**(5), 2003, pp. 733–735.

[5] NOMURA K., OHTA H., UEDA K., KAMIYA T., HIRANO M., HOSONO H., *Thin-film transistor fabricated in single-crystalline transparent oxide semiconductor*, Science **300**(5623), 2003, pp. 1269–1272.

[6] CARCIA P.F., MCLEAN R.S., REILLY M.H., NUNES G., *Transparent ZnO thin-film transistor fabricated by rf magnetron sputtering*, Applied Physics Letters **82**(7), 2003, pp. 1117–1119.

[7] ROBERTSON J., *High dielectric constant oxides*, The European Physical Journal – Applied Physics **28**(3), 2004, pp. 265–291.

[8] ROBERTSON J., *High dielectric constant gate oxides for metal oxide Si transistors*, Reports on Progress in Physics **69**(2), 2006, pp. 327–396.

[9] ROBERTSON J., *Band offsets of wide-band-gap oxides and implications for future electronic devices*, Journal of Vacuum Science and Technology B **18**(3), 2000, pp. 1785–1791.

[10] WILK G.D., WALLACE R.M., ANTHONY J.M., *High-κ gate dielectrics: current status and materials properties considerations*, Journal of Applied Physics **89**(10), 2001, pp. 5243–5275.

[11] MOORE G.E., *Cramming more components onto integrated circuits*, Electronics **38**(8), 1965, pp. 114–117.

[12] SHIH-HSIEN H. LO, BUCHANAN D.A., YUAN TAUR, WEN I. WANG, *Quantum-mechanical modeling of electron tunneling current from the inversion layer of ultra-thin-oxide nMOSFET's*, IEEE Electron Device Letters **18**(5), 1997, pp. 209–211.

[13] SUNTOLA T., ANTSON J., *Method for Producing Compound Thin Films*, U.S. Patent 4,058,430, 1977.

[14] GIERAŁTOWSKA S., SZTENKIEL D., GUZIEWICZ E., GODLEWSKI M., ŁUKA G., WITKOWSKI B.S., WACHNICKI Ł., ŁUSAKOWSKA E., DIETL T., SAWICKI M., *Properties and characterization of ALD grown dielectric oxides for MIS structures*, Acta Physica Polonica A **119**(), 2011, pp. 692–695.

[15] BIERCUK M.J., MONSMA D.J., MARCUS C.M., BECKER J.S., GORDON R.G., *Low-temperature atomic--layer-deposition lift-off method for microelectronic and nanoelectronic applications*, Applied Physics Letters **83**(12), 2003, pp. 2405–2407.

[16] GIERALTOWSKA S., WACHNICKI L., WITKOWSKI B.S., GODLEWSKI M., GUZIEWICZ E., *Atomic layer deposition grown composite dielectric oxides and ZnO for transparent electronic applications*, Thin Solid Films **520**(14), 2012, pp. 4694–4697.

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