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# Wet thermal oxidation of GaAs and GaN

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## 1. Introduction

The chapter is devoted to the thermal wet oxidation of III-BV semiconductor compounds, mainly to gallium arsenide and gallium nitride. It has been divided into several topics, containing of monoclinic gallium oxide<sup>1</sup>  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> properties data, techniques of oxide fabrication and application description. In the first part, properties of mentioned semiconductor's oxides are characterized. Then methods of manufacturing with a special attention for wet thermal oxidation are described. After that, applications of gallium oxide structures in electronics are given. It focuses also on the semiconductor structures dedicated for gas sensors application while gallium oxide layers improve significantly the most critical parameters of the detector compared to those containing of e.g. SnO<sub>2</sub>.

III-BV and III-IN semiconductor compounds are wide known as materials for optoelectronics devices. They are used often also to the construction of high temperature and microwave devices or chemical gas sensors. In these applications dielectric layers are necessary. There is a possibility of using their own oxides – Ga<sub>2</sub>O<sub>3</sub> gives a chance to manufacture many different devices – MOS structures (Metal-Oxide-Semiconductor). It can be MOS capacitors, power Metal Oxide Semiconductor Field Effect Transistors (MOSFETs), high mobility GaAs MOSFETs or gate turn-off thyristors and, probably, CMOS applications (Pearton et al., 1999; Wu et al., 2003). The MOS-gate version of the HEMT has significantly better thermal stability than a metal-gate structure and is well suited to gas sensing (Schweben et al., 1998; Baban et al., 2005; Hong et al., 2007).

## 2. Properties of $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

Gallium oxide  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is a wide band gap material that ensures deep-UV transparency. Appropriately doped could reach conductive properties thus is included to the TCO's (transparent conductive oxides) materials like ITO or ZnO which are the state-of-the-art materials in optoelectronics.

Gallium oxide occurs in various structures like  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\sigma$ ,  $\varepsilon$  types (Kim & Kim, 2000). Among many polymorphs, monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is considered to be the equilibrium phase (Battiston et al., 1996; Chen et al., 2000; Vázquez et al., 2004). It is stable thermally and chemically

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<sup>1</sup> The typical name for Ga<sub>2</sub>O<sub>3</sub> are: digallium trioxide, gallium(III) oxide, gallium trioxide, gallium oxide. We use in the text term: gallium oxide.

(Battiston et al., 1996; Vı́llora et al., 2004). The thermal stability of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> reaches nearly melting point reported as 1740 °C (Orita et al., 2004) and 1807 °C (Tomm et al., 2000) or 2000 K (Vı́llora et al., 2004) what determines also possibility of working at high temperature.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> in monoclinic structure has a elemental unit dimensions as follows: a=12.214 Å, b=3.0371 Å, c=5.7981 Å and  $\beta$ =103.83° (Tomm et al., 2000) or a=12.23 Å, b=3.04 Å, c=5.8 Å and  $\beta$ =103.7° (Vı́llora et al., 2004). Cleavage along (100) plane (Tomm et al., 2000; Ueda a et al., 1997; Vı́llora et al., 2004) and (001) (Vı́llora et al., 2004) are highly preferred. The space group of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is C2/m (C<sub>32h</sub>) where GaO<sub>6</sub> share octahedral sites along b and are connected by GaO<sub>4</sub> tertrahedra thus anisotropy of optical as well as electrical properties is expected depending on the direction to the chains – perpendicular or parallel (Ueda b et al., 1997). The  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> unit cell along b, c and a-axis could be found in (Vı́llora et al., 2004).

2.1 Electrical properties

At room temperature  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is an insulating material, above 500 °C has a semiconductor properties (Fleischer & Meixner, 1993; Battiston et al., 1996; Frank et al., 1996; Orita et al., 2004). Although electrically conductive crystals of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> have been also reported, see Table 1 (Vı́llora et al., 2004).

direction	resistivity	mobility	carrier concentration
	Ω·cm	cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>	cm <sup>-3</sup>
<100>	0.11	83	7x10 <sup>17</sup>
<010>	0.19	78	4x10 <sup>17</sup>
<001>	0.08	93	9x10 <sup>17</sup>

Table 1. Electrical properties measured for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystal along certain direction

2.1.1 Electrical conductance

The tetravalent tin ion Sn<sup>4+</sup> is most often chosen as a donor dopant (Orita et al., 2000; Orita et al., 2004) because its ionic radius is close to that of Ga<sup>3+</sup> and simultaneously Sn<sup>4+</sup> ions prefer sixfold coordination. This causes substituting of Ga<sup>3+</sup> octahedral sites and results in formation of shallow donors (Orita et al., 2004). Additionally formation of oxygen vacancies in the layer provides an occurrence of shallow levels as reported for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals (Ueda a et al., 1997). Thus much emphasize has been placed on the optimization of the deposition process conditions. Alteration of ambient atmosphere and substrate temperature in e.g. PLD (Pulsed Lased Deposition) technology had significant impact on the properties of the layer. In order to assure formation of oxygen vacancies and doping by Sn<sup>4+</sup> low partial pressure of oxygen and elevation of substrate temperature to 880 °C were applied. It could increase chemical potential of oxygen in the lattice what introduces oxygen vacancies and solution of tin ions to the lattice. Reported mobility of carriers was 0.44 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and maximum electrical conductivity 1.0 S·cm<sup>-1</sup>. These parameters were achieved for layers deposited on substrates maintained at 880 °C under pressure equal to 6x10<sup>-5</sup> Pa. Increase of oxygen pressure to 1.3x10<sup>-2</sup> Pa led to lowering of conductivity to 3.6x10<sup>-3</sup> S·cm<sup>-1</sup> (Orita et al., 2000). This effect was confirmed by Ueda et al. (Ueda b et al., 1997) for crystals obtained in floating zone technique; increase of oxygen flow rate significantly affected electrical conductivity of investigated material (see Fig. 1(a)). Under O<sub>2</sub> atmosphere undoped crystals were insulating

$\sigma < 10^{-9} \Omega^{-1}\text{cm}^{-1}$ . With addition of  $\text{N}_2$  to the atmosphere the conductivity increased and reached  $0.63 \Omega^{-1}\text{cm}^{-1}$ . However the  $\text{N}_2$  content in the growth ambient is limited by the stability of crystals (Ueda a et al., 1997). The maximum obtained electrical conductivity was  $38 \Omega^{-1}\text{cm}^{-1}$  for sample grown in gas mixture of  $\text{N}_2/\text{O}_2$  with partial pressure ratio of 0.4/0.6. To achieve enhancement in conductivity of gallium oxide also  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  donor dopants in polycrystalline films for application in gas sensors were used (Frank et al., 1996). Unexpected only slight increase in conductivity and decrease in sensitivity were obtained. Thus  $\text{SnO}_2$  doping was applied by Frank et al. The highest conductivity was reached for 0.5%  $\text{SnO}_2$  (see Fig. 1 (b)). Doping possibility seems to be restricted due to solution in lattice limit (Frank b et al. 1998).

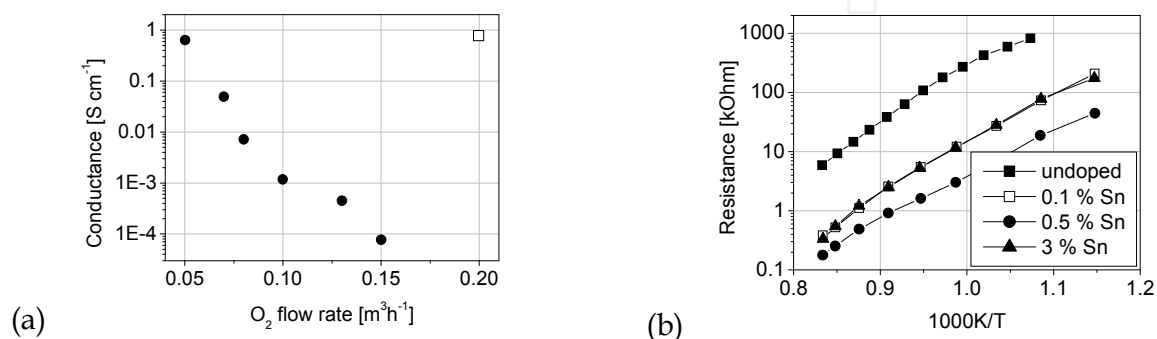


Fig. 1. (a) Electric conductivity of the  $\beta\text{-Ga}_2\text{O}_3$  single crystals along the b-axis as a function of the  $\text{O}_2$  flow rate. The closed circles - samples grown from undoped  $\text{Ga}_2\text{O}_3$  rods; open square - sample grown from Sn-doped  $\text{Ga}_2\text{O}_3$  rods (Ueda a et al., 1997); (b) Resistance in wet synthetic air of undoped and  $\text{SnO}_2$  doped thin films (Frank b et al., 1998)

Depending on orientation, crystals grown in floating zone technique, had resistivities as follows:  $0.11 <100>$ ,  $0.19 <010>$  and  $0.08 <001> \Omega\cdot\text{cm}$  (Villora et al., 2004) and those obtained by Ueda et al. were  $0.026 \Omega\cdot\text{cm}$  (b-axis) and  $0.45 \Omega\cdot\text{cm}$  (c-axis) (Ueda b et al., 1997). Conductivity did not depend on temperature in the range of 0 – 300 K as shown in Fig 2.

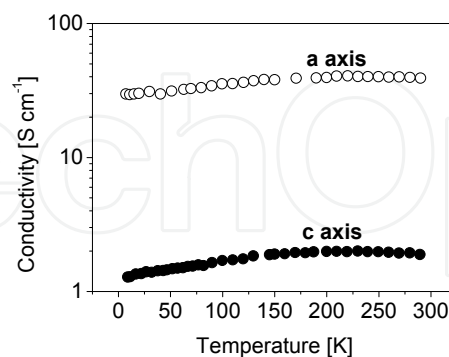


Fig. 2. Temperature dependence of the electrical conductivity along b- and a -axis of  $\beta\text{-Ga}_2\text{O}_3$  single crystals (Ueda b et al., 1997)

The  $\text{Mg}^{2+}$  was used as an acceptor dopant by Frank et al. (Frank et al., 1996) to achieve conversion to p-type semiconductive material from intrinsic n-type. Layers sequence consisting of dopant and  $\text{Ga}_2\text{O}_3$  was deposited on quartz glass substrates by reactive sputtering and subsequently annealed at temperatures up to  $1200^\circ\text{C}$ . Strong decrease of

conductivity was observed, but values of this parameters were comparable for 0.3 and 3% of MgO what indicated on achievement of solubility limit already by 0.3% of MgO.

Bulk crystals of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> are electrically conductive but achievement of conductive layers has required many efforts. Application of proper substrate is crucial. The octahedral Ga<sup>3+</sup> chains are responsible for generating paths for electrons thus growth of (-201)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> in which b axis is parallel to the substrates are considered as promising (Orita et al., 2004). This requirement could be fulfilled by application of (0006) Al<sub>2</sub>O<sub>3</sub> substrates.

### 2.1.2 Carriers mobility

Villora et al. have measured carriers mobilities of three different oriented samples. Results were 83, 78 and 98 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for <100>, <010> and <001> directions, respectively (Villora et al., 2004). Proper optimization of process in floating zone technology led to the achievement of carrier mobility of 46 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for single crystals (Ueda et al., 1997). Electron mobility in single crystals and polycrystalline, inhomogeneous, porous ceramics of Ga<sub>2</sub>O<sub>3</sub> was also investigated by M. Fleischer et al. at temperature from 800 °C to 1000 °C as in this range gas sensors operate (Fleischer & Meixner, 1993). Electron mobility determined from Hall measurement was nearly the same for both samples - 10 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. Also increase of mobility was observed with increasing the temperature of measurement. Ueda et al. (Ueda et al., 1997) have measured mobilities along b and c directions for floating zone obtained (100) platelets. Mobility along b direction was of one order of magnitude larger than that for c direction. Obtained values were as follows: 46 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> (b-axis) and 2.6 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> (c-axis).

### 2.1.3 Dielectric constant and breakdown field

Dielectric constant of gallium oxide is rather rarely investigated. Value reported in (Zhou et al., 2008) is of about 10.2. Shan et al. (Shan et al., 2005) have measured dielectric constant for thin layers deposited on p-Si (100) and sapphire (0001) substrates by PEALD (Plasma Enhanced Atomic Layer Deposition). Substrates temperature during the process was maintained at 200 °C. As-deposited layers were amorphous and had large leakage current. Annealing at 700 or 900 °C has improved that parameter but simultaneously layers dielectric constants decreased. Figure 3 presents dielectric constants of as-deposited and annealed at various temperatures Ga<sub>2</sub>O<sub>3</sub> thin films.

The breakdown field/voltage depends significantly on technology of fabrication of the material. Values reported for thermally oxidized layers were 0.05-0.1 MV/cm (Readinger et al., 1999), 0.65 MV/cm (Zhou et al., 2008), 1 MV/cm (Lin et al., 2006) and 3.85 MV/cm (Kim et al., 2001) when those for PEALD were 1-1.5 MV/cm (Shan et al., 2005) and e-beam evaporation 3.6 MV/cm (Passlack et al., 1995).

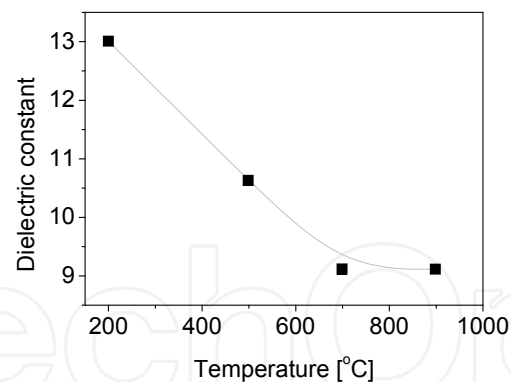


Fig. 3. Dielectric constants of as-deposited Ga<sub>2</sub>O<sub>3</sub> thin film and of those annealed at various RTA temperatures (Shan et al., 2005)

2.2 Optical properties

Gallium oxide is highly transparent in visible and near UV range of wavelengths (Villora et al., 2004). Transmittances in the range of visible light and UV range exceeding 80% were reported by (Matsuzuki et al., 2006; Orita et al., 2004; Ueda b et al., 1997) and that reaching nearly 100% by (Shan et al., 2005). Enhancement of transmittance could be obtained by increase of oxide layer deposition temperature (Orita et al., 2004; Orita et al., 2000) or appropriate annealing of crystals (Ueda a et al., 1997).

Because of the anisotropy of optical properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> the absorption edge depends on the angle of incident beam of light to the c or b direction of the crystal. Assuming that  $\varphi$  is an angle between c-axis and electric field vector E Ueda et al. have investigated the transmission of floating zone obtained (001)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> platelets with thickness of 0.159 mm (Ueda 2 et al., 1997). Figure 4 (a) presents the optical transmission spectra of an insulating  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> for various  $\varphi$ . The dichroism of the transmission spectra is remarkable. It was also indentified by Tippins (Tippins, 1965) and Ueda (Ueda a et al., 1997) which observed absorption edge at 255 nm and additional shoulder at 275 nm. The explanation of the dichroism could be found at (Ueda b et al., 1997).

Band gap energy  $E_g$  of gallium oxide varies in a wide range from 4.23 to 5.24 eV depending on the parameters of applied technology, see Table 2 and Fig. 4 (b). One of the parameters influencing the band gap is temperature of annealing of deposited layer Fig. 4 (b).

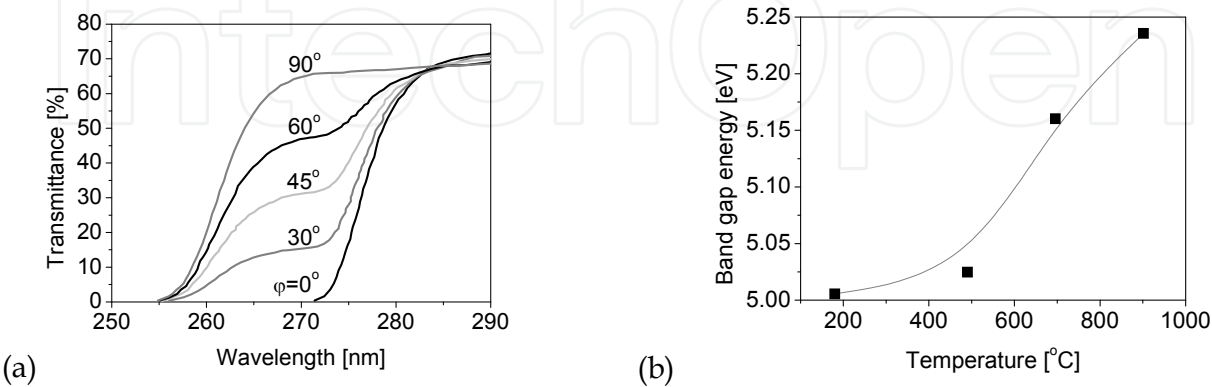


Fig. 4. (a) Optical transmission spectra of an insulating  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> for various  $\varphi$  (Ueda b et al., 1997) and (b) band gap energy of the as-deposited Ga<sub>2</sub>O<sub>3</sub> and annealed at various temperatures thin films (Shan et al., 2005)



Refractive indexes of gallium oxide are generally in the range of 1.8-1.9. Ueda et al. have reported in (Ueda a et al., 1997) for single crystals values of 1.84 and 1.88 at 980 nm, those for e-beam evaporated layers were 1.841-1.885 at 980 nm (Passlack et al., 1995), for PEALD 1.89 (Shan et al., 2005), and for bulk 1.91 (Passlack et al., 1995).

E <sub>g</sub> (eV)	substrate	technology	reference
5.04	fused silica	e-beam evaporation under oxygen partial pressure of 5x10 <sup>-4</sup> mbar	(Al-Kuhaili et al. 2003)
5.00	Al <sub>2</sub> O <sub>3</sub> (0001)	plasma enhanced ALD	(Shan et al. 2005)
4.9	α-Al <sub>2</sub> O <sub>3</sub> , silica	PLD	(Matsuzuki et al. 2006) (Orita et al. 2000)
4.84	fused silica	e-beam evaporation with no excess of oxygen	(Al-Kuhaili et al. 2003)
4.79	-	floating zone (along b-axis)	(Ueda b et al. 1997)
4.75	quartz	spray pyrolysis	(Hao & Cocivera 2002)
4.74	Si (001)	rf magnetron sputtering	(Rebien et al. 2002)
4.72	GaAs	e-beam evaporation	(Rebien et al. 2002)
4.6	-	Czochralski	(Tomm et al. 2000)
4.52	-	floating zone (along c-axis)	(Ueda b et al. 1997)
4.48	quartz	spray pyrolysis (annealed at 600 °C)	(Hao & Cocivera 2002)
4.44	quartz	spray pyrolysis (annealed at 900 °C)	(Hao & Cocivera 2002)
4.23	borosilicate glass	spray pyrolysis	(Kim & Kim 2000)

Table 2. Bang gap energy values of gallium oxide for various techniques

2.3 Crystalline quality and morphology

Depending on deposition technology gallium oxide layers are generally amorphous as reported for samples obtained by PEALD (Shan et al., 2005), MOVPE (Metalorganic Vapor Phase Epitaxy) (Battiston et al., 1996; Kim & Kim, 2004) or PLD (Orita et al., 2004). Crystallization of films could be assured by its annealing at high temperature (Battiston et al., 1996; Kim & Kim, 2004; Shan et al., 2005), increase of substrates temperature (Orita et al., 2004) or oxidation at high temperatures. For example amorphous layers of β-Ga<sub>2</sub>O<sub>3</sub> deposited on (0001) Al<sub>2</sub>O<sub>3</sub> substrates in PLD at 325 °C were obtained by Orita et al.. Diffraction peaks appeared in layers deposited at temperatures above 380 °C (Orita et al., 2004). In case of CVD (Chemical Vapor Deposition) β-Ga<sub>2</sub>O<sub>3</sub> layers annealing process at temperatures above 700 °C assured crystallization.

Crystalline properties of gallium oxide are usually determined based on XRD (X-Ray Diffraction) with CuK<sub>α</sub> radiation measurement of 2θ patterns. The most commonly appearing peaks are (-202), (400) and (-111) at 2θ angle of about 100°, 54° and 17° (Battiston et al. 1996) or (11-3) and (30-6) at 39° and 59° (Chen et al., 2000) as well as (-206) and (-306) at 49.6° and 59.1° (Kim et al., 2001). Except of crystallites directions determination, XRD method is applied to the estimation of crystallites sizes. For this purpose broadening of peak widths is investigated and Sherrer formula applied. Crystallites sizes are usually in the range from 20 to 50 nm (Battiston et al., 1996; Frank et al., 1996) and could be enlarged by temperature of annealing increase. The root mean square of layers varies in the range from 5 to 25 Å. Reported values were as follows: 5 Å (Shan et al., 2005), 8-13 Å (Wolter et al., 2000), 10-20 Å (Matsuzaki et al., 2006) and 12-23 Å (Kim & Kim, 2004).

There is a variety of other parameters of oxides apart from those described and analyzed above. Authors refer to photoluminescence studies to (Hao & Cocivera, 2002), density of interface states (Lin et al., 2005; Lin et al., 2006; Nakano b et al., 2003; Zhou et al., 2008) or oxidation states as well as etching behavior (Passlack et al., 1995).

### 3. Fabrication of the gallium oxide layers

There are several methods of manufacturing of gallium oxide for semiconductor devices applications. One can, after C.W. Wilmsen (Wilmsen, 1985), say that the main ways are: (a) chemical oxidation, (b) thermal oxidation, (c) anodic oxidation, (d) plasma oxidation, and (e) other methods. Dry or wet thermal oxidation are also applied. Since several years bulk crystals of  $\text{Ga}_2\text{O}_3$  are available (Tomm et al., 2000; V1llora et al., 2004) as well.

Thermal oxidation of AIIIBV and AIIIN compounds – dry (Wilmsen, 1985; Lin et al., 2000) or wet (Readinger et al., 1999) – is unfortunately not similar to silicon oxidation. It is caused by other structure – these compounds consist of two or more elements which variously react with oxygen and water. In addition, AIIIBVs and AIIINs are very thermodynamically unstable – especially As and N have high partial pressures. In spite of these difficulties in many laboratories one carry on thermal oxidation studies because this technique is relatively cheap and can give good results. The most known is AlAs oxidation for diode lasers (especially VCSEL lasers), electroluminescent diodes and detectors with Bragg reflectors (Geib et al., 1997; Pucicki et al., 2004).

#### 3.1 Chemical oxidation

Typical chemical oxidizers for GaAs are  $\text{HNO}_3$  with  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$ . Chemical oxidation method is used as a part of surface GaAs substrates cleaning and rather is not used for making gallium oxide layers for devices (Ghidaoui, 2002).

#### 3.2 Electrochemical (anodic) oxidation

Oxidation of semiconductors electrochemical anodic process is similar to typical process of oxide layer manufacturing in electrolyte. Anodic process is more efficient if in semiconductor materials holes occur – type p of electrical conduction. For type n it is necessary to generate holes in order to facilitate oxidation. The easier way is illumination by the appropriate light – with photon energy in the range from 1.4 eV to 5 eV (Wilmsen, 1985). The level of the photon energies depends on energy bandgap of the semiconductor.

The process is simple in the theory. Problems appear with increasing of the oxide thickness – both, electrical resistivity of oxide layer and diffusion rate of the oxidizing factor in the layer are variable. Problem that could appear is a choice of the appropriate electrolyte – it depends on the material, anodic equipment etc. One should to make electrical contacts to the semiconductor: permanent or temporary, which have to be stable in the applied electrolyte. Oxides after anodic process of GaAs are a mixture of gallium and arsenic oxides. These layers are not tight and ought to be annealed in high temperature (more than 450 °C). At this temperature arsenic oxides dissociate and gallium oxide will remain crystalline.

The anodic oxidation of n-type GaN (1.7  $\mu\text{m}$  thick layer on sapphire substrate with carrier concentration of  $4.6 \times 10^{18} \text{ cm}^{-3}$ ) under laboratory illumination at a constant current density of  $5 \text{ mA}\cdot\text{cm}^{-2}$  in sodium tungstate electrolyte ( $0.1 \text{ MNa}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ ) at 298 K was made by



Pakes et al. (Pakes et al., 2003). They have observed local oxidation and that the oxidation has occurred at troughs in the faceted GaN layers. Near the peaks in the faceted surface oxidation was negligible. The localized nature of the oxidation of the GaN is presumed, after authors, to be related to the strength of the Ga-N bond and non-uniform distributions of impurity, non-stoichiometry or defects in the substrate (Pakes et al., 2003). The oxide was non-uniform and textured with pore-like features. The absence of a compact anodic film is probably due to extensive generation of nitrogen during anodic oxidation which disrupts development of a uniform anodic film.

Peng et al. (Peng et al., 2001) have patented the method of nitride material oxidation enhanced by illumination with UV light at room temperature. Authors used 254-nm UV light to illuminate the GaN crystals to generate electron-hole pairs. The pH value of the electrolyte was in the range of approximately 3 to 10, preferably about 3.5. The authors (Peng et al., 2001) claim that: *"This invention allows the rapid formation of gallium oxide at room temperature, and it is possible to monitor the thickness of the oxide in-situ by means of measuring the loop current."*

### 3.3 Plasma oxidation

By plasma oxidation of GaAs gaseous plasma containing oxygen are used. The sources of oxygen are  $O_2$ ,  $N_2O$  or  $CO_2$ , and it is excited by a RF coil (Wilmsen, 1985; Hartnagel & Riemenschnieder, 1999). A DC bias oxidation takes place in a similar way to the wet anodization process. In the oxide layers without thermal treatment  $Ga_2O_3$  and  $As_2O_3$  almost in equal proportions were found. Ions which attacked substrate can sputter the surface, and thus lead to a reduced growth rate and to a modification of surface stoichiometry due to a preferential sputtering of the arsenic component (Hartnagel & Riemenschnieder, 1999). The plasma parameters (RF frequency, RF power and gas pressure) may not affect the oxide growth, but they do affect the degree of GaAs surface degradation during the initial stage of oxide formation. In contrast, wet anodic oxidations give almost damage-free oxides.

### 3.4 Dry thermal oxidation

Dry thermal oxidation processes of GaAs and GaN are carried out in ambient of oxygen or mixture of nitrogen and oxygen. Dry oxidation of GaAs is made rather seldom. Processes are very complicated because of problems with arsenic and its low thermal stability. Typical top oxide layers on GaAs surface consist of mixture:  $Ga_2O_3 + GaAsO_4 + As_2O_3$  and are rough. Near the interface of oxide-gallium arsenide occur  $Ga_2O_3$  and elemental As (after: Wilmsen, 1985). These layers are amorphous. By higher oxidation temperature (above 500 °C) oxides are polycrystalline and also rather rough. They contain mainly  $Ga_2O_3$  but  $GaAsO_4$  was also observed. The elemental As, small crystallites of  $As_2O_5$  and  $As_2O_3$  appeared in layers as well (after: Pessegi et al., 1998). Arsenic oxides have low thermal stability and during annealing processes oxides undergo decomposition releasing arsenic which escapes from the samples.

Thermal oxidation of GaAs technique has more than thirty years. Thermal oxidation of GaN epilayers is a considerably younger – it is a matter of last ten years.

Gallium nitride needs higher temperature as GaAs or AlAs: typical range of dry oxidation is between 800 and 1100 °C (Chen et al., 2000). Processes are carried out usually in atmosphere of oxygen (Chen et al., 2000; Lin et al., 2006). Chen et al. (Chen et al., 2000) described several

experiments with GaN layers on sapphire substrates. Authors made oxidation of GaN samples in dry oxygen. Time of oxidation was changed from 20 min to 8 h by the flow of  $O_2$  of about 1 slm. Temperature was changed from 800 to 1100 °C. They have observed two different courses for temperatures of over 1000 °C: very rapid oxidation process in the initial stage of oxidation and then, after about 1 h, followed by a relatively slow process. Authors have deliberated after Wolter et al. (Wolter et al., 1998) the reaction rate constant and have concluded that in the first step of oxidation (rapid process) the oxide creation reaction is limited by the rate of reaction on GaN-oxide interface. In second step (slow process by thicker oxide layers) the oxide creation reaction is determined by the diffusion-controlled mechanism (transition from reaction-controlled mechanism to the diffusion-controlled mechanism). They have supposed GaN decomposition at high temperature (over 1000 °C) which can speed up the gallium oxidation (Chen et al., 2000). The authors also have observed volume increase of about 40% after oxidation.

Similar experiments were made by Zhou et al. (Zhou et al., 2008) by oxidation of GaN powder and GaN free-standing substrates with Ga-terminated surface (front side) from HVPE epitaxial processes. They have used dry oxygen as a reactor chamber atmosphere only and have changed time (from 4 to 12 hours) and temperature (850, 900, 950 and 950 °C) of oxidation. According to authors, oxidation rate in temperature below 750 °C is negligible. They have made similar analysis as Chen et al. (Chen et al., 2000) after Wolter et al. (Wolter et al., 1998) and observed similar dependence of the oxide thickness versus time process. In GaN dry oxidation processes one could observe two zones: interfacial reaction-controlled and diffusion-controlled mechanism for low and high temperature, respectively (Zhou et al., 2008). Authors of this paper have wrote about “*thermally grown gallium oxide on (...) GaN substrate*”. It is typical for many authors although all of them described oxidation process.

### 3.5 Wet thermal oxidation

Problems in wet thermal oxidation of GaAs processes are very similar to those which occur during dry oxidation. Arsenic in GaAs has low thermal stability in high temperature and it is rather difficult to carry out oxidation process at the temperature higher than 600 °C. The applied temperatures from the range below 600 °C gave not rewarding results. The obtained by Korbutowicz et al. (Korbutowicz et al., 2008) gallium oxide layers have been very thin and had have weak adhesion.

Processes of wet thermal GaN oxidation are carried out more often. Gallium nitride has better thermal stability than gallium arsenide and one can apply higher temperature to obtained  $Ga_2O_3$  is thicker and has better parameters.

Typical apparatus for wet thermal oxidation of GaAs or GaN is very similar to that which is applied to wet thermal oxidation of AlAs or  $Al_xGa_{1-x}As$ . It can be: Closed Chamber System CCS (a) or Open Chamber System OCS (b). The open systems are more often used as the systems with closed tube one.

#### 3.5.1 Close chamber systems

Choe et al. have described in their paper (Choe et al., 2000) CCS equipment for AlAs oxidation which was schematically depicted in Figure 5 a. It also can be applied to GaAs oxidation. The quartz reaction (oxidation) chamber had two temperature zones – the upper and lower zone, one for the sample and second for the water source. It was small chamber –

3 cm in diameter by 30 cm in length. Typical amount of water was about 2 cm<sup>3</sup>. Chamber with sample and water was closed and the air was evacuated using a pump. After this hermetically closed chamber was inserted into a furnace. During the heating, water was expanded as a vapour and filled whole volume of the quartz ampoule. Typical temperature in the upper zone was 410 °C and in the lower zone was varied from 80 °C to 220 °C. In this apparatus the oxidation process is controlled by two parameters: temperature of oxidation and temperature of water source.

These systems have some advantages: reaction kinetics is controlled by two temperatures: oxidation and water vapour creation, there is a small demand of oxidizing agent – water and no carrier gas. A considerable inconvenience is the necessity of vacuum pumps application.

### 3.5.2 Open chamber systems

Open chamber system for GaAs and GaN oxidation looks like silicon oxidation system. It consists of horizontal (very often) quartz tube, water bubbler and source of the gases: carrier – nitrogen N<sub>2</sub> or argon Ar and (sometimes) oxygen O<sub>2</sub> (Choquette et al., 1997; Readinger et al., 1999; Pucicki et al., 2004; Geib et al., 2007; Korbutowicz et al., 2008). The three-zone resistant furnace works as a system heating (Fig. 5 b). Korbutowicz et al. (Korbutowicz et al., 2008) have used the bubbler (in the heating jacket with a temperature control) with deionized water H<sub>2</sub>O as a source of oxidizing agent and nitrogen N<sub>2</sub> as a main gas and the initial water level was the same in all experiments to keep the same conditions of the carrier gas saturation.

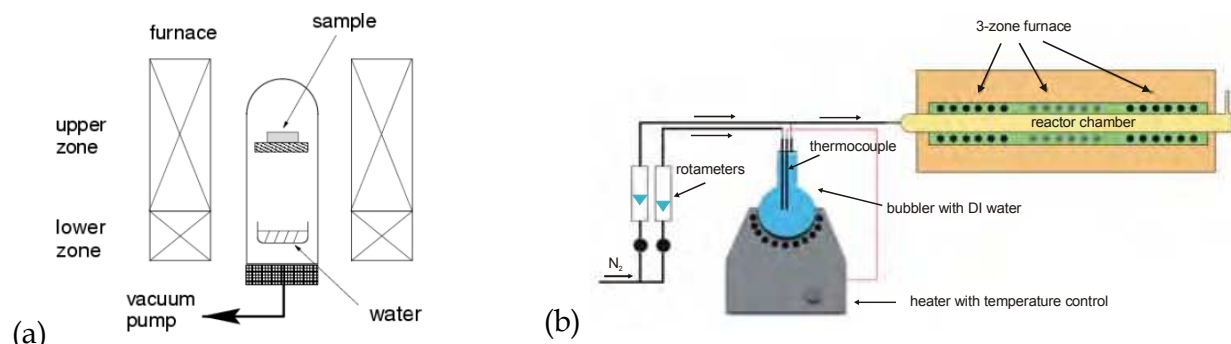


Fig. 5. (a) A schematic diagram of the CCS for wet thermal oxidation (Choe et al., 2000); (b) typical apparatus for GaAs and GaN wet thermal oxidation

The open systems are cheaper as the closed ones. The work with the OCS's are more complicated – one need to take into consideration numerous parameters: source water temperature, reaction temperature, main gas flow and flow of the carrier gas through the bubbler, kind of gases and using or not of oxygen. The significant water consumption during oxidation and the requirement of the water source temperature stabilization also constitute problems. But the valuable advantage of open systems is their simple construction.

Thermal wet oxidation method as a more frequently applied way to get gallium oxide layers will be wider described now.

Reaction kinetics of thermal wet oxidation and reaction results depend on several parameters: a zone reaction temperature (a), a water source temperature (water bubbler) (b),

a flow of a main carrier gas (c), a flow of a carrier gas through the water bubbler (d), time of the reaction (e) and type of carrier gas (f).

Korbutowicz et al. (Korbutowicz et al., 2008) have described processes of the GaAs and GaN thermal wet oxidation – GaAs wafers and GaN layers manufactured by MOVPE and HVPE (Hydride Vapor Phase Epitaxy) on sapphire substrates were used in these studies. GaAs in form of bare wafers (one side polished, Te doped) or wafers with epilayers (Si doped) were employed in investigations. A range of oxidation temperature was between 483 and 526 °C. Time was varied from 60 to 300 minutes. Typical main flow of nitrogen was 2 800 sccm/min and typical flows through the water bubbler were 260 and 370 sccm/min.

Thicknesses of the gallium oxides layers grown on gallium arsenide substrates surface were uneven – it was visible to the naked eye: one can observe variable colors on the surface (see Fig. 6 (a)). Defects are preferable points to create oxide – from these spots started the oxidation process (Fig. 6 (b)). Authors were able to obtain thin layers only, since by longer process duration oxide layers were cracked and exfoliated. In Fig. 6 (c) one can see that oxide layers were thin and transparent. Occurring cracks show that in interface region of GaAs-oxide exists a considerable strain.

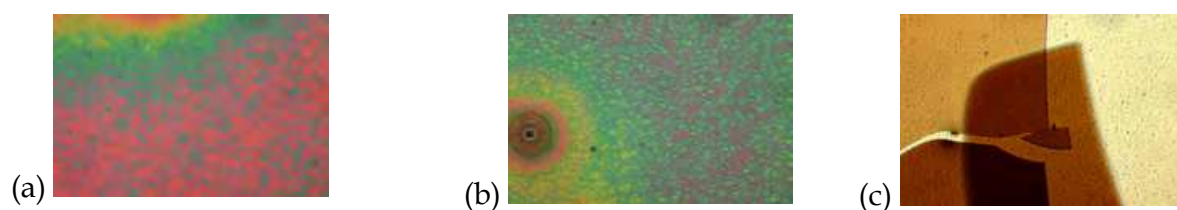


Fig. 6. Views of oxide surface's layers from optical microscope: variable colors of gallium oxide (a); substrate's defect and oxide (b); cracked and exfoliated oxide layer (c)

Two kinds of GaN samples have been used – GaN epilayers deposited on sapphire substrates – thin layers from MOVPE and thick layers from HVPE with surface as grown. Temperature of oxidation was higher as for GaAs samples and was as follows: 755, 795 and 827 °C. Typical water temperature was 95 or 96 °C. The main flows of nitrogen were varied from 1 450 to 2 800 sccm/min and the flows through the water bubbler were altered from 260 to 430 sccm/min. The total gas flow in the reactor chamber was about 3 000 sccm/min.

In order to determine suitable parameters, temperature of water source and temperature of reaction (oxidation) zone were changed. Gas flows and time of the process were varied also. The obtained thicknesses of gallium oxide were from several nanometers up to hundreds of nanometers. The MOVPE GaN layers has much more smoother surface as from HVPE ones. The influence of this difference one can remark after oxidation.

Optical observations by using naked eyes and optical microscope gave a lot of information about morphology of surface with oxide. One can observe (Fig. 7.) e.g. smoothing of GaN hexagonal islands. Wet oxidation of gallium arsenide appeared to be more difficult than that of GaN. The  $\text{Ga}_2\text{O}_3$  layers which were obtained by Korbutowicz et al. were heterogeneous (see below results from X-ray diffraction – Fig. 8).



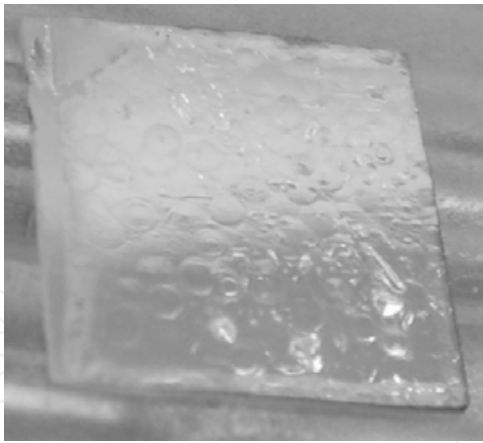


Fig. 7. HVPE GaN layer surface after wet thermal oxidation

Figure 8. shows x-ray spectrum of gallium compounds on sapphire substrate (G32 sample). One can remark that oxidized surface layer contained GaN, Ga<sub>2</sub>O<sub>3</sub> and Ga<sub>x</sub>NO<sub>y</sub>.

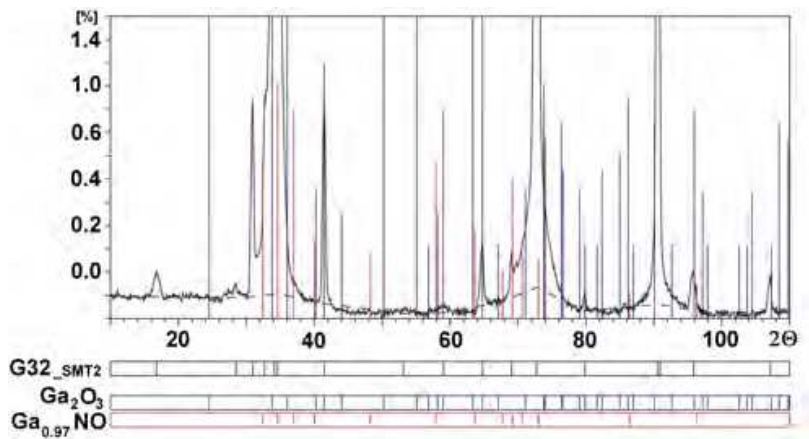


Fig. 8. X-ray diffraction spectrum of oxidized GaN on sapphire from HVPE; G32\_SMT2 - spectrum from thick GaN layer

The MOVPE GaN crystals had smoother surface as HVPE crystals and were more resistant for oxidation. In Figure 9 results of AFM (Atomic Force Microscope) observations of the surface and profile of MOVPE sample, thickness of 880 (nm) (a) and HVPE sample, thickness of 12 (μm) (b) are shown. Both samples were oxidized in the same conditions: reaction temperature of 827 °C, water source temperature of 95 °C, process time of 120 min and the same water vapour concentration. The initial surface of MOVPE sample was smooth, while the surface of HVPE thick layers was rather rough. The oxidation process was faster by HVPE crystals because at these crystals surfaces was more developed. The surface of oxidized GaN from MOVPE remained smooth, whereas on the surface of the sample from HVPE one could observe typical little bumps.

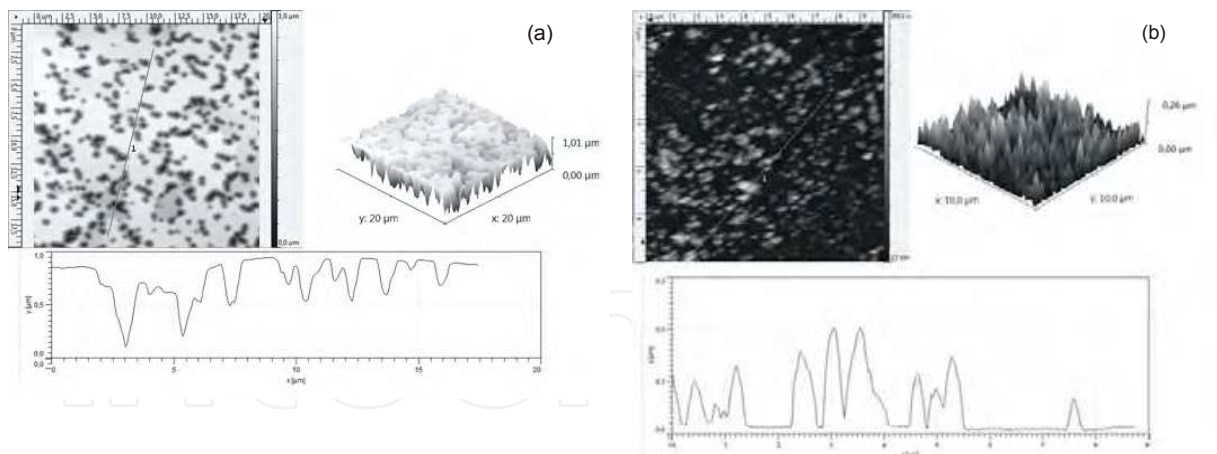


Fig. 9. AFM images of the surface of GaN<sub>(MOVPE)</sub> sample (a) and GaN<sub>(HVPE)</sub> sample (b)

Readinger et al. (Readinger et al., 1999) have carried out processes applying GaN powder and GaN thick layers on sapphire from vertical HVPE. Atomic percentage of water vapor in carrier gas (O<sub>2</sub>, N<sub>2</sub>, and Ar) was maintained on the same level (77%±8%) for all furnace temperatures (700, 750, 800, 850 and 900 °C) and carrier gas combinations. For comparison purposes authors have prepared a dry oxidation processes (in dry oxygen) for the same samples. Sample's surfaces after wet oxidation were much smoother as from dry process. The authors have observed that below 700 °C in which GaN has a good stability in oxidizing environments. They also have found that in ambient of oxygen (dry or wet) the oxidation had faster rate as in wet nitrogen or argon atmosphere. Thicknesses of gallium oxide layers in wet O<sub>2</sub> process revealed linear dependence on duration of oxidation. Wet oxidation have given even poorer electrical results than dry oxidation. The authors have judged that electrical parameters deterioration aroused from very irregular morphology at the wet oxide/GaN interface.

### 3.6 Other oxidation methods

These above mentioned oxidation methods are not the only ways to get gallium oxide. There are several others ones:

- ion-beam induced oxidation (after: Hartnagel & Riemenschnieder, 1999),
- laser assisted oxidation (Bermudez, 1983),
- low-temperature oxidation (after: Hartnagel & Riemenschnieder, 1999),
- photowash oxidation (Offsay et al., 1986),
- oxidation by an atomic oxygen beam (after: Hartnagel & Riemenschnieder, 1999),
- UV/ozone oxidation (after: Hartnagel & Riemenschnieder, 1999),
- vacuum ultraviolet photochemical oxidation (Yu et al., 1988).

### 3.7 Summary

Apart from above mentioned methods are several other ways to obtain or manufacture gallium oxide layers. One can deposited by Chemical Vapour Deposition CVD, Physical Vapour Deposition PVD or Physical Vapour Transport PVT methods. One can use Local Anodic Oxidation LAO by applying AFM equipment (Matsuzaki et al., 2000; Lazzarino et al., 2005; Lazzarino et al., 2006) to GaAs or GaN surface oxidizing and creating small regions



covered by gallium oxide. As was told earlier in chapter 2, the best parameters for semiconductor devices has monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. This type of oxide is easy to obtain by thermal oxidation: dry or wet. These methods also give possibility to selective oxidation using dielectric mask (e.g. SiO<sub>2</sub>). Despite the difficulties and problems on account of numerous process parameters which ought to be taken into consideration, wet thermal oxidation of GaAs and GaN processes seem to be the best way for making oxide layers for devices applications.

#### 4. Applications of gallium oxide structures in electronics

Due to existent of native silicon oxide domination of silicon in electronics lasts many years. Semiconductor compounds as AIIIBV or AIIIN have very good parameters which just predestine to work in a region of high frequencies and a high temperature with a high power: insulating substrates, high carrier mobility and wide bandgap. These all give a big advantage over Si and their alloys. But silicon still dominates. Why?

SiO<sub>2</sub> is an amorphous material which does not bring strain in underlying silicon. Gallium arsenide GaAs applied in semiconductor devices technology has cubic crystal structure (as other AIIIBV compounds) and typical surface orientation (100). Gallium oxide with monoclinic structure, which is the only variety of Ga<sub>2</sub>O<sub>3</sub> stable in high temperature that stays stable after cooling, is strongly mismatched to GaAs. It causes bad relationships between GaAs epitaxial layers and oxide. In addition, gallium oxide growth on a surface of gallium arsenide is in a reality a mixture of Ga<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>5</sub> and elemental As, as was mentioned above. This mixture is unstable at elevated temperature and has poor dielectric parameters. In order to avoid problems with the growth of Ga<sub>2</sub>O<sub>3</sub> on GaAs surface some of researches have applied thin dielectric layer of Al<sub>2</sub>O<sub>3</sub> in GaAs MOSFET structure (e.g. Jun, 2000) but it is not a matter of our consideration.

By GaN oxidation is other situation than by GaAs treatment. Gallium nitride applied in electronics has hexagonal structure and is better matched. GaN, in comparison to GaAs, is more chemical, thermal and environmental resistant. Therefore nitrides are more often used to construction of numerous devices with a oxide-semiconductor structure: MOS diodes and transistors, gas and chemical sensors.

Silicon electronics supremacy was a result of, among others, applying of silicon oxide SiO<sub>2</sub> possibility. Properties of interface silicon oxide and silicon are just excellent. This fact allows manufacturing of very-large scale integration circuits with Complementary Metal Oxide Semiconductor (CMOS) transistors (Hong, 2008). But silicon devices encounter difficulties going to nanoscale – very thin dielectric gate layers is too thin and there is no effect: charge carriers can flow through the gate dielectric by the quantum mechanical tunnelling mechanism. Leakage current is too high – Si devices need dielectrics with higher electrical permittivity  $k$ . Also power devices made from silicon and their alloys operate in smaller range of power and frequency. One can draw a conclusion: MOS devices need high  $k$  gate dielectric and carriers with higher mobility in channels of transistors as in silicon's ones. Whole microelectronics requires something else, for example indium phosphide, diamond, silicon carbide, gallium arsenide or gallium nitride and their alloys (see Fig. 10 (Kasu, 2004)).

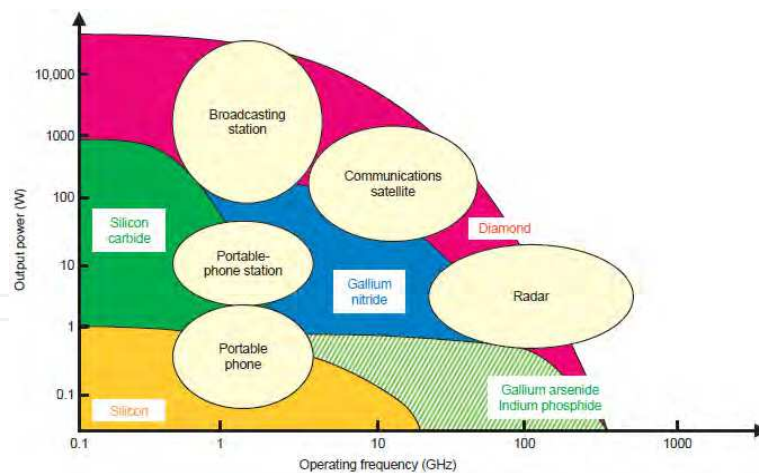


Fig. 10. Demand for high-frequency high-power semiconductors to support the rise in communication capacity (Kasu, 2004)

Despite very good properties, AIIIBV and AIIIN have problems to become commonly used, especially in power applications. A big obstacle is a lack of high quality stable gate dielectrics with high value of dielectric constant. In opinion Ye (Ye, 2008): “*The physics and chemistry of III–V compound semiconductor surfaces or interfaces are problems so complex that our understanding is still limited even after enormous research efforts.*” and that can be the purpose although first GaAs MOSFETs was reported by Becke and White in 1965 (after: Ye, 2008) still there are problems with wide scale production.

One can deposit silicon dioxide, silicon nitride and similar dielectrics but these materials have relatively small dielectric constant.  $\text{SiO}_2$  has dielectric constant equal to 3.9,  $\text{Si}_3\text{N}_4$  has constant = 7.5, but silicon nitride is not easy in a treatment. Typical value of dielectric constant given in literature for  $\text{Ga}_2\text{O}_3$  is in a range from 9.9 to 14.2 (Passlack et al., 1995; Pearton et al., 1999).

#### 4.1 Metal Oxide Semiconductor devices

The first thermal-oxide gate GaAs MOSFET was reported in the work of Takagi et al. in 1978 (Takagi et al., 1978). The gate oxide, which has been grown by the new GaAs oxidation technique in the  $\text{As}_2\text{O}_3$  vapor, was chemically stable. Oxidation process was carried out in a closed quartz ampoule. Temperature of liquid arsenic trioxide was equal to 470 °C and temperature of GaAs (gallium oxide growth) was 500 °C. Authors supposed that this method can be used in large scale as a fabrication process. But up to now it is not the typical manufacture technique.

Typical GaAs MOSFET has the gate dielectric in the form of oxides mixture:  $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ . This mixture comes not from oxidation but from UHV deposition (e.g. Passlack, et al. 1997; Hong et al., 2007; Passlack et al., 2007). Practically almost all papers of Passlack’s team from the last twenty years have described oxide structures this type:  $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$  which were made in UHV apparatus.

Difficulties with obtaining good  $\text{Ga}_2\text{O}_3$  layers on GaAs from thermal oxidation inclined researches to make GaAs MOS structures with oxidized thin layer of AlGaAs or InAlP but then aluminium is oxidized, not gallium (e.g. Jing et al., 2008).

Matter of the GaN MOS structures looks similar and different too. In many cases gate dielectric is Gadolinium Gallium Garnet (GGG)  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  called also Gadolinium Gallium

Oxide (GGO), a synthetic crystalline material of the garnet group or  $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$  (e.g. Gila et al., 2000) as by GaAs MOSFETs. Some researches tried to make  $\text{Ga}_2\text{O}_3$  layer on GaN as dielectric film for MOS applications: MOS capacitors (Kim et al., 2001; Nakano & Jimbo, 2003) or MOS diodes (Nakano et al., 2003).

Kim et al. (Kim et al., 2001) were studied dry thermal oxidation of GaN in ambient of oxygen. It was a furnace oxidation at 850 °C for 12 h which resulted in the formation of monoclinic  $\beta\text{-Ga}_2\text{O}_3$  layer, 88 nm in thickness. Authors have analyzed the structural properties of the oxidized sample by SEM (scanning electron microscopy), XRD and AES (Auger Electron Spectroscopy) measurements. In order to develop the electrical characteristics of the thermally oxidized GaN film, a MOS capacitor was fabricated. Based on observations and measurements, authors have found that: (i) the formation of monoclinic  $\beta\text{-Ga}_2\text{O}_3$  occurred, (ii) the breakdown field strength of the thermal oxide was  $3.85 \text{ MVcm}^{-1}$  and, (iii) the C-V curves showed a low oxide charge density ( $N_f$ ) of  $6.77 \times 10^{11} \text{ cm}^{-2}$ . After Kim et al. it suggests that the thermally grown  $\text{Ga}_2\text{O}_3$  is promising for GaN-based power MOSFET applications (Kim et al., 2001).

Nakano & Jimbo (Nakano & Jimbo, 2003) have described their study on the interface properties of thermally oxidized n type GaN metal-oxide-semiconductor capacitors fabricated on sapphire substrates. A 100 nm thick  $\beta\text{-Ga}_2\text{O}_3$  was grown by dry oxidation at 880 °C for 5 h. After epitaxial growth, authors have made typical lateral dot-and-ring  $\beta\text{-Ga}_2\text{O}_3/\text{GaN}$  MOS capacitors by a thermal oxidation method. In order to reach this aim a 500 nm thick Si layer was deposited on the top surface of the GaN sample as a mask material for thermal oxidation. Formation of monoclinic  $\beta\text{-Ga}_2\text{O}_3$  was confirmed by XRD. They have also observed from SIMS (secondary ion mass spectrometry) measurements, an intermediate Ga oxynitride layer with graded compositions at the  $\beta\text{-Ga}_2\text{O}_3/\text{GaN}$  interface (see Fig. 11). The presence of GaNO was remarked by Korbutowicz et al. (Korbutowicz et al., 2008) in samples from the wet thermal oxidation after XRD measurements as well. Nakano & Jimbo (Nakano & Jimbo, 2003) have not observed in the C- t and DLTS (Deep Level Transient Spectroscopy) measurements discrete interface traps. They have judged that it is in reasonable agreement with the deep depletion feature and low interface state density of  $5.53 \times 10^{10} \text{ eV}^{-1}\text{cm}^{-2}$  revealed by the C-V measurements. They have supposed that the surface Fermi level can probably be unpinned at the  $\beta\text{-Ga}_2\text{O}_3/\text{GaN}$  MOS structures fabricated by a thermal oxidation technique. The authors have compared as well the sputtered  $\text{SiO}_2/\text{GaN}$  MOS and  $\beta\text{-Ga}_2\text{O}_3/\text{GaN}$  MOS samples in DLTS measurements. In Fig. 12 results of this study were shown. In contrast to the  $\beta\text{-Ga}_2\text{O}_3/\text{GaN}$  MOS structure,  $\text{SiO}_2/\text{GaN}$  MOS sample has a large number of interface traps may induce the surface Fermi-level pinning at the MOS interface, resulting in the capacitance saturation observed in the deep depletion region of the C-V curve (Nakano & Jimbo, 2003).

In slightly later publication of Nakano et. al. (Nakano et al., 2003) have described electrical properties of thermally oxidized p-GaN MOS diodes with  $n^+$  source regions fabricated on  $\text{Al}_2\text{O}_3$  substrates. Oxide was grown in the same way as in paper (Nakano & Jimbo, 2003). Results obtained by authors in this study have suggested that the thermally grown  $\beta\text{-Ga}_2\text{O}_3/\text{p-GaN}$  MOS structure is a promising candidate for inversion-mode MOSFET.

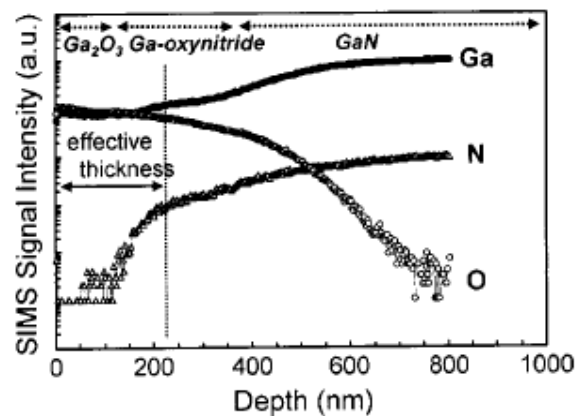


Fig. 11. SIMS profiles of Ga, N, and O atoms in the thermally oxidized  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>/GaN MOS structure (Nakano & Jimbo, 2003).

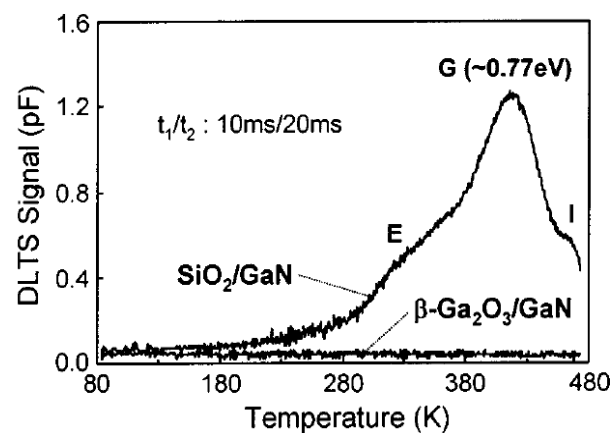


Fig. 12. Typical DLTS spectra at a rate window  $t_1/t_2$  of 10 ms/20 ms for the thermally oxidized  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>/GaN MOS and sputtered SiO<sub>2</sub>/n-GaN MOS structures after applying the bias voltage of 225 V (Nakano & Jimbo, 2003).

Lin et al. (Lin et al., 2006) have studied the influence of oxidation and annealing temperature on quality of Ga<sub>2</sub>O<sub>3</sub> grown on GaN. GaN wafers were oxidized at 750 °C, 800 °C and 850 °C. Authors have measured the electrical characteristics and interface quality of the resulting MOS capacitors have compared. The process steps for making GaN MOS capacitor is shown in Fig. 13. The 300-nm SiO<sub>2</sub> layer was deposited on the GaN surface by radio-frequency sputtering to play as a mask for oxidation.

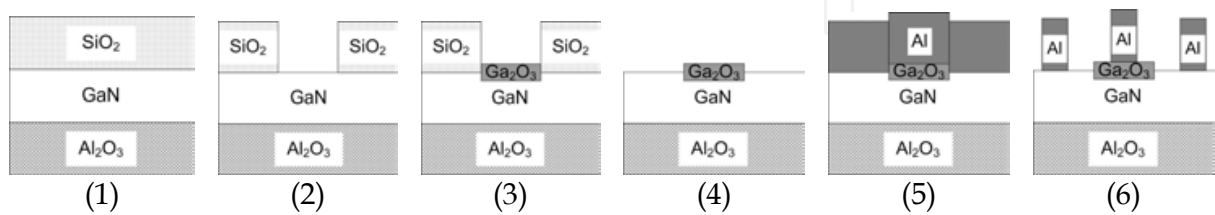


Fig. 13. Process flow for GaN MOS capacitor (Lin et al., 2006)

Oxidation was carried out in dry oxygen ambient and followed by a 0.5 h annealing in argon at the same temperature as oxidation. GaN oxidized at a higher temperature of 850 °C

presented better interface quality because less traps were formed at the interface between GaN and the oxide due to more complete oxidation of GaN at higher temperature. But the best current-voltage characteristics and C-V characteristics in accumulation region and surface morphology had the sample from 800 °C oxidation process (Lin et al., 2006).

4.2 Gas sensors

Metal oxides Ga<sub>2</sub>O<sub>3</sub> gas sensors operating at high temperatures are an alternative for widely used SnO<sub>2</sub> based sensors. Both types of sensors are not selective but react for a certain group of gasses depending on the temperature of operation. Responses on oxygen, NO, CO, CH<sub>4</sub>, H<sub>2</sub>, ethanol and acetone are most often investigated. Ga<sub>2</sub>O<sub>3</sub> sensors exhibit faster response and recovery time, and lower cross-sensitivity to humidity than SnO<sub>2</sub> based sensors, see Fig. 14 (Fleischer & Meixner, 1999). Additional advantages are long-term stability and no necessity of pre-ageing. Ga<sub>2</sub>O<sub>3</sub> sensors show stability in atmospheres with low oxygen content what make them suitable for exhaust gas sensing. There is also no necessity of degassing cycles in contrary to SnO<sub>2</sub> sensors. Disadvantages are lower sensitivity and higher power consumption due to high temperature operation (Hoefer et al., 2001).

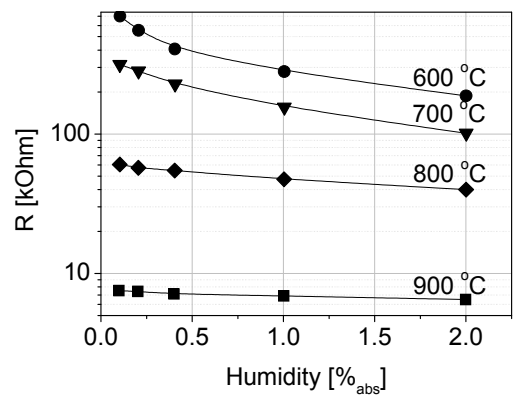


Fig. 14. Temperature dependence of the effect of humidity on the conductivity of Ga<sub>2</sub>O<sub>3</sub> thin films, measured in synthetic air (Fleischer & Meixner, 1999)

Typical structure of a gas sensor consists of interdigital electrode (Fig. 16. Type A) (usually platinum) deposited on the sensing layer composed of polycrystalline Ga<sub>2</sub>O<sub>3</sub> with grain sizes of 10 and 50 nm (Fleischer a et al., 1996) or 50–100 nm (Schwebel et al., 2000; Fleischer & Meixner et al., 1995).

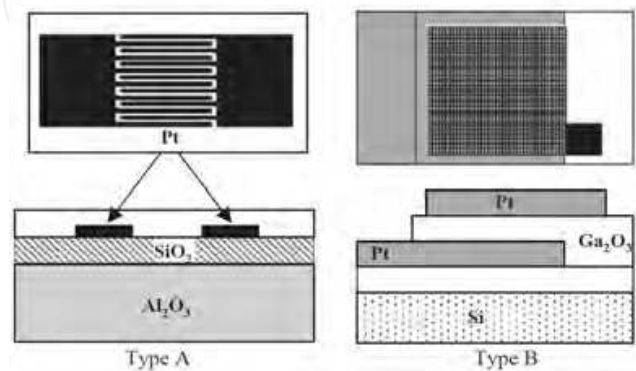


Fig. 15. Typical interdigital oxide sensor (Type A) and modified mesh structure (Type B) (Baban et al., 2005)



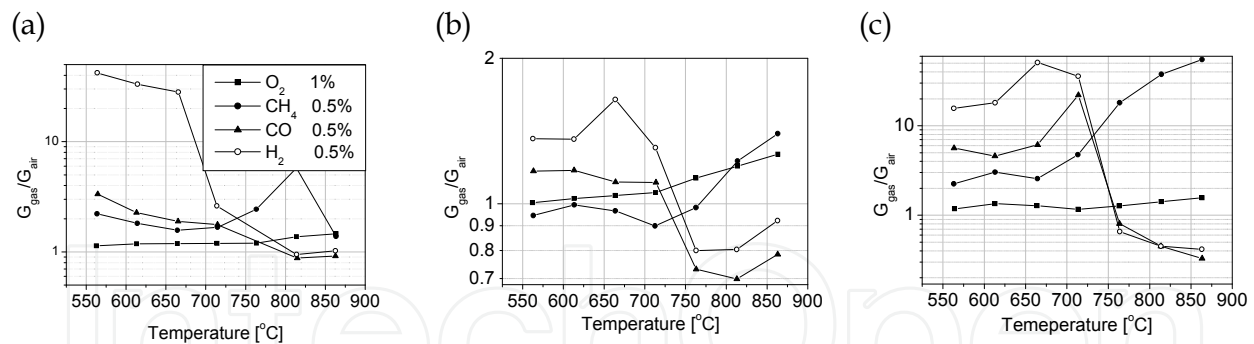


Fig. 16. Comparison of the gas sensitivity of three different morphologies of  $\beta\text{-Ga}_2\text{O}_3$ : (a) single crystals, (b) bulk ceramics with closed pore structure, and (c) polycrystalline thin film (Fleischer & Meixner, 1999)

However, sensitivities of three different morphologies of  $\beta\text{-Ga}_2\text{O}_3$  as single crystals, bulk ceramics with closed pore structure and polycrystalline thin film were also investigated (see Fig. 16) (Fleischer & Meixner, 1999).

Baban et al. proposed sandwich structure with double  $\text{Ga}_2\text{O}_3$  layer and mesh double Pt electrode layer (Fig. 15. Type B), nevertheless, that device did not achieve neither higher sensitivity nor fast response time, but it helped to conclude about the mechanism of detection (Baban et al., 2005). The most commonly applied fabrication technique is sputtering of thin  $\text{Ga}_2\text{O}_3$  and its subsequent annealing in order to achieve crystallization of the layer. Although low-cost, screen printed, thick  $\text{Ga}_2\text{O}_3$  layers with sensing properties similar to that based on thin layers could be also used (Frank et al., 1998).

Sensing mechanism is assumed to be based on charge carrier exchange of adsorbed gas with the surface of the sensing layer. Resistance modulation is a consequence of the change of free charge carrier concentration resulted from the alteration of acceptor concentration on the surface raising from the reaction of molecules with adsorbed oxygen ions when exposed to oxygen containing ambient (Hofer et al., 2001).

Generally adsorbed reducing or oxidizing gas species inject electrons into or extract electrons from semiconducting material (Li et al., 2003) thus changing material conductivity. Gallium oxide exhibits gas sensitivity at temperature range from 500 °C to 1000 °C. At lower temperatures reducing gases sensitivity occurred. In the range from 900 °C to 1000 °C the detection mechanism is bound to  $\text{O}_2$  defects equilibrium in the lattice (Fleischer et al., 1996).

Modification of sensor parameters, such as sensitivity, selectivity (cross-sensitivity) and response as well as recovery times for certain gas, could be assured by three ways: temperature modulation, deposition of appropriate filter layer/clusters on the active layer or by its doping. As described in (Fleischer et al., 1995) gallium oxide layers of 2  $\mu\text{m}$  deposited by sputtering technique (grain sizes typically 50-100 nm) exhibited response to reducing gases in the range of 500 – 650 °C of operating temperatures. Increase of temperature caused decrease of the sensitivity to these gases and simultaneous enhancement of response to  $\text{NH}_4$ . Temperatures of 740 – 780 °C assured suppression of reducing gases sensitivity leading to the selectivity to  $\text{NH}_4$ .

Cross-sensitivity of ethanol and other organic solvents to methane were restricted by application of filter layer of porous  $\beta\text{-Ga}_2\text{O}_3$  deposited on thin sensing  $\text{Ga}_2\text{O}_3$  layer Fig. 17 (Flingelli et al., 1998).



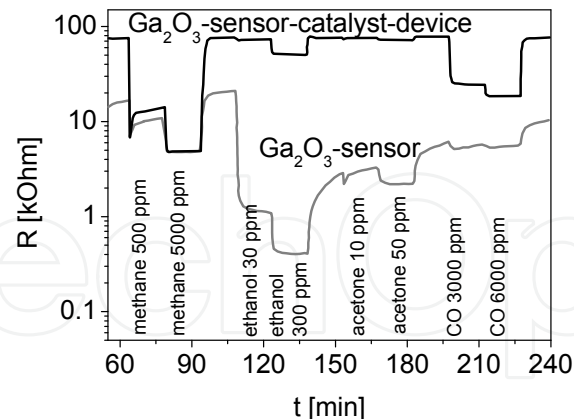


Fig. 17. Response of a pure  $\text{Ga}_2\text{O}_3$  sensor and a sensor catalyst device (hybrid research type) to methane, ethanol, acetone and CO in wet synthetic air at 800 °C (Flingelli et al., 1998)

Fleischer et al. (Fleischer b et al., 1996) have investigated application of amorphous  $\text{SiO}_2$  layer covering  $\text{Ga}_2\text{O}_3$  on the sensitivity, selectivity and stability of hydrogen sensor. Polycrystalline, 2  $\mu\text{m}$  thick gallium oxide layers were deposited by sputtering technique and subsequently heated at 850 °C for 15 hours or 1100 °C for 1 hour. Crystallites sizes were 10 and 50 nm, respectively. Sensors sensitivity was investigated for: NO (300 ppm by vol.), CO (100 ppm by vol.),  $\text{CH}_4$  (1% by vol.),  $\text{H}_2$  (1000 ppm by vol.), ethanol (15 ppm by vol.) and acetone (15 ppm by vol.) In order to avoid cross-sensitivity the measurements were prepared in 0.5% of humidity; also influence of humidity reduction to 0.025% by vol. as well as  $\text{O}_2$  content from 20 to 1% was evaluated. Uncoated  $\text{Ga}_2\text{O}_3$  sensor responded by decrease of the conduction of the layer for reducing gases. At lower temperatures stronger response was to more chemically reactive gases in contrary to higher temperatures where significant response to chemically stable gasses was observed. Detection time of  $\text{H}_2$  strongly depended on the operating temperature of the sensor. Response time at 600 °C was 10 min and 30 s at above 700 °C. Temperatures of 900 °C and above assured rapid decrease in conductivity of layer. All responses were reversible. To prevent the formation of oxygen on the  $\text{Ga}_2\text{O}_3$  surface during the oxidation process, what would exclude this kind of layers from the application for  $\text{H}_2$  sensing, additional  $\text{SiO}_2$  layers were used. Use of 30 nm  $\text{SiO}_2$  layer caused lowering of response to reducing gases at temperatures of 900 °C and below, except of  $\text{H}_2$ . The optimal operation temperature for  $\text{H}_2$  detection was 800 °C. Silicon dioxide layers of 300 nm thick have suppressed responses to all gasses at all temperatures except to  $\text{H}_2$ . In this case optimal temperature of operation was 700 °C. Gallium oxide sensor with  $\text{SiO}_2$  cap layer could be used as a selective, high temperature hydrogen sensor (Fleischer b et al., 1996). To assure of oxygen selectivity in oxygen-rich atmospheres Schwebel et al. (Schwebel et al., 2000) have applied catalytically active oxides. Modification materials like  $\text{CeO}_2$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  were deposited on the surface of 2  $\mu\text{m}$  thick  $\text{Ga}_2\text{O}_3$  sputtered on ceramic substrates and annealed at 1050 °C for 10 hours (crystallite sizes 50–100 nm). Sensors with surface modified by  $\text{La}_2\text{O}_3$  or  $\text{CeO}_2$  responded only to oxygen changes in the ambient, in contrary to uncoated  $\text{Ga}_2\text{O}_3$  sensor, which reacts with variety of gases. Modification of the surface with  $\text{Mn}_2\text{O}_3$  caused insensitivity to any gases and thus could be used as reference sensor for

compensation of temperature influence in double sensor construction because of similar values of thermal activation energy for conduction (Schwebel et al., 2000).

Gallium oxide sensors are sensitive for strongly reducing gases. Thus detection of  $\text{NO}_3$ ,  $\text{NH}_3$  or  $\text{CO}_2$  is considerably restricted. To investigate their influence on the selectivity various layers like  $\text{Ta}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{NiO}$ ,  $\text{AlVO}_4$ ,  $\text{SrTiO}_2$ ,  $\text{TiO}_2$  and  $\text{Ta}_2\text{O}_3$  were deposited on properly prepared sensors consisting of 2  $\mu\text{m}$  thick gallium oxide obtained by sputtering technique and subsequently annealed. Application of  $\text{TiO}_2$  and  $\text{SrTiO}_2$  did not improve the selectivity to  $\text{O}_2$  or eliminate the cross-sensitivity to reducing gases. Modification of the surface with  $\text{WO}_3$  gave a strong reaction to  $\text{NH}_3$  at 600 °C and  $\text{NO}$  at 350 °C compared to bare  $\text{Ga}_2\text{O}_3$ . In case of  $\text{NiO}$  coating suppression of reaction with methane was revealed at 600-700 °C. That effect could be used as a reference in double sensor construction. Using of  $\text{AlVO}_4$  assured selectivity for  $\text{O}_2$  when operating at 700 °C and insensitivity to gases at temperature above 900 °C (Fleischer et al., 1996).

Lang et al. have applied modification of  $\text{Ga}_2\text{O}_3\text{:SnO}_2$  sensing layer surface by iridium, rhodium and ruthenium clusters. Ruthenium modified layers exhibited significant increase of response on ethanol, when iridium modified sensor demonstrated enhanced sensitivity to hydrogen at lower operating temperature. Sensitivity was 80 at 550 °C (3000 ppm  $\text{H}_2$ ) compared to unmodified sensor which sensitivity was 20 at 700 °C (3000 ppm  $\text{H}_2$ ). Measurements of as low concentration as 30 ppm were possible. Rhodium modified sensor could be used only as a detector of presence of ethanol (Lang et al., 2000).

Dopants such as  $\text{ZrO}_2$ ,  $\text{TiO}_2$  and  $\text{MgO}$  were applied in sandwich structure of sensor containing as follows: substrate/Pt interdigital structure/ $\text{Ga}_2\text{O}_3$ /dopant/ $\text{Ga}_2\text{O}_3$ /dopant/ $\text{Ga}_2\text{O}_3$  in order to investigate their influence on the sensitivity. However, no influence on the sensitivity to  $\text{O}_2$  was reported. Additionally, response decrease to  $\text{CH}_4$  for  $\text{ZrO}_2$  doping and slight increase for  $\text{MgO}$  doping was observed (Frank et al., 1996).

Sensitivity to  $\text{CO}$  and  $\text{CH}_4$  was achieved by application of  $\text{SnO}_2$  doping in the sandwich structure. The highest response was for 0.1% at. for both gases. However no influence of doping on oxygen sensitivity was observed (Frank et al., 1998).

Responses on oxygen of  $\text{Ga}_2\text{O}_3$  semiconducting thin films doped with Ce, Sb, W and Zn were investigated by Li et al. 2003 (Li et al., 2003). Films doped with Zn exhibited the largest responses for gas concentrations as follows: 100 ppm, 1000 ppm and 10000 ppm. The optimum operation temperature was 420 °C. On the other hand Ce doped gallium oxide samples responded promptly to the gas induced. The reaction time was less than 40 s, when that for Zn doped layer was 100 s. Baban et al. have obtained response times on oxygen of 14 and 27 s for ordinary interdigital platinum structure and newly proposed sandwich structure, respectively (Baban et al., 2005). Li et al. have also investigated stability and repeatability of the sensors. Responses of all sensors were relatively reproducible, see Fig. 18 (Li et al., 2003).

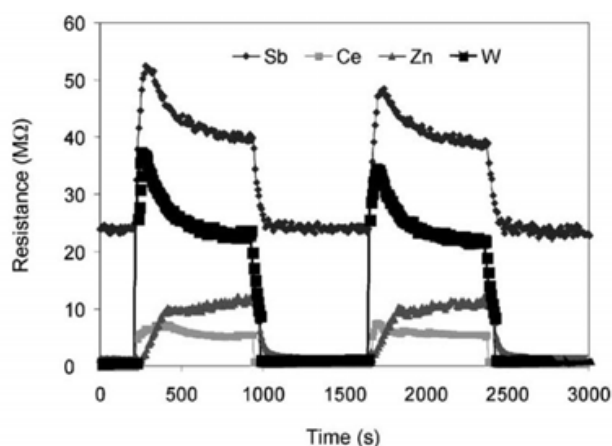


Fig. 18. Electrical response of doped  $\text{Ga}_2\text{O}_3$  films at temperature of 500 °C (1000 ppm  $\text{O}_2$ ) (Li et al., 2003)

Sensors doped with Sb and W after exposure to the analyzed gas exhibited initial growth of resistance followed by its exponential decrease.

## 5. Conclusion

Gallium oxide appeared to be a good candidate for optoelectronic and electronic applications. Intrinsic  $\text{Ga}_2\text{O}_3$  layers have insulating nature, but after appropriate modification could reach conductive parameters. Very interesting effect is n-type semiconducting behavior at elevated temperatures originating from oxygen deficiencies in  $\text{Ga}_2\text{O}_3$ . Gallium oxide is a material included to the group of transparent conductive oxides (TCOs) that are of great interest. Among all TCOs, e.g. ITO or  $\text{ZnO}$ ,  $\beta\text{-Ga}_2\text{O}_3$  has the largest value of band-gap what assures high transparency in the range from visible to deep-UV wavelengths. Additionally  $\beta\text{-Ga}_2\text{O}_3$  is chemically and thermally stable. That all advantages make  $\beta\text{-Ga}_2\text{O}_3$  to be intensively investigated although there is a lot of issues that should be researched.

In the chapter main focus was placed on the monoclinic gallium oxide and its most widely applied fabrication methods. There is also a large part devoted to the application of that material. Metal Oxide Semiconductor transistors and gas sensors, based on pure and doped gallium oxide, principles of operation and parameters were described.

Parameters of  $\text{Ga}_2\text{O}_3$  chosen to the analysis and discussion were selected concerning possible application of that material. Influence of parameters of process of layers deposition or crystal growth on the electrical as well as optical parameters of gallium oxide was included. Possible ways of modification of layers properties are also embraced.

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