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Impedance Spectroscopic Study of β-Ga_2O_3/O_2 Interaction

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Impedance spectroscopy was used to study the oxygen/oxide-semiconductor interaction mechanism using sputtered β-Ga_2O_3/SiO_2/Al_2O_3 and β-Ga_2O_3/BeO thin-layer sensor structures between 578 and 850°C. The total sample resistance was composed of its bulk (R_b) and its grain boundary resistance (R_{gb}). While for the β-Ga_2O_3/BeO sample R_{gb} is dominant in the entire temperature range, for the β-Ga_2O_3/SiO_2/Al_2O_3 structure at higher temperatures it roughly equals R_b. The adsorption of oxygen influenced rather the grain boundary resistance than the bulk resistance. The oxygen sensitivity of β-Ga_2O_3 proved to be frequency dependent; applying a certain frequency it exceeded the dc sensitivity.

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In the case of oxide-semiconductor-based chemical gas sensors, the dc measurements do not give information on the mechanism of processes. However, the ac method offers a powerful tool to examine the nature of the conduction processes and the mechanism of the gas/solid interactions.

β-Ga_2O_3 single-crystal[1] and polycrystalline[2,3] samples were examined in the medium-frequency range. Authors could distinguish the electronic and ionic conduction as a function of temperature.

In this work it is shown that starting from low frequencies (10 mHz), impedance spectroscopy is suitable for distinguishing the effect of gas on the bulk resistance and grain boundary resistance of a polycrystalline β-Ga_2O_3 sample.

Experimental

In the experiments two types of sandwich structures were used. In the first case a 2 μm thick β-Ga_2O_3 film was sputtered on an Al_2O_3 substrate on which a SiO_2 diffusion barrier layer was previously formed. Its role was to prevent the interdiffusion of β-Ga_2O_3 and Al_2O_3. The 1 μm thick Pt interdigital contact structure was placed between the barrier and the oxide semiconductor layer. In the second case the oxide semiconductor layer was directly sputtered on the BeO substrate.

Figure 1. SEM micrograph of a sputtered β-Ga_2O_3 film after a 1 h annealing at 1100°C.

Before the experiments each sample was annealed for 1 h, at 1100°C, in air in order to obtain the necessary grain size and vacancy concentration. The typical grain size, shown in Fig. 1, is about 100 nm.[4]

The ac and dc conductance were measured as a function of the temperature (578-850°C) in (20% O_2 + N_2) and (1% O_2 + N_2) gas mixtures, respectively. The sample was heated by a Pt heater deposited on the back side of the substrate. The temperature was controlled using a pyrometer.

The ac frequencies varied between 10 mHz and 100 kHz. Below 12 Hz the impedance was measured by dual-beam storage oscilloscope, while at high frequencies a General Radio 1689 Precision RLC Digibridge instrument was used. The I-V (current-voltage) plots were also registered.

Results and Discussion

The Nyquist diagrams of the β-Ga_2O_3/SiO_2/Al_2O_3 sample were measured in a (20% O_2 + N_2) gas mixture at 578°C (Fig. 2) and at 835°C (Fig. 3), respectively. For the evaluation of the experimental results, several equivalent circuits are reported in the literature. The one proposed by Macdonald[5] is shown in Fig. 4. Here R_1 corresponds to the bulk resistance, while C_1 represents the geometric capacitance. R_2 and C_2 characterize the metal oxide semiconductor (Schottky) contact, while R_3 and C_3 stand for the space-charge regions formed on the grain boundaries. It is reported[6] that the polycrystalline samples show an anomalous behavior as a function of frequency. The circuit element known as constant-phase element (CPE)

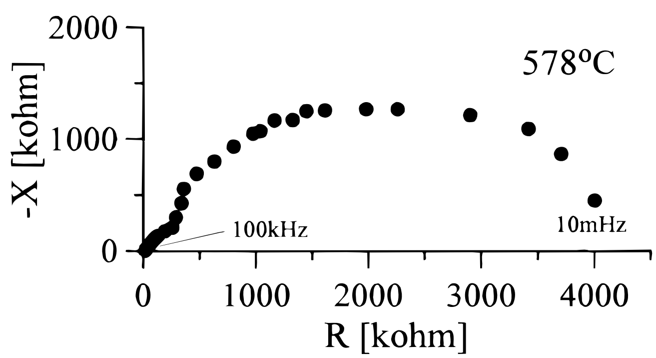

Figure 2. Impedance spectrum of a β-Ga_2O_3/SiO_2/Al_2O_3 sample at 578°C in dry air.

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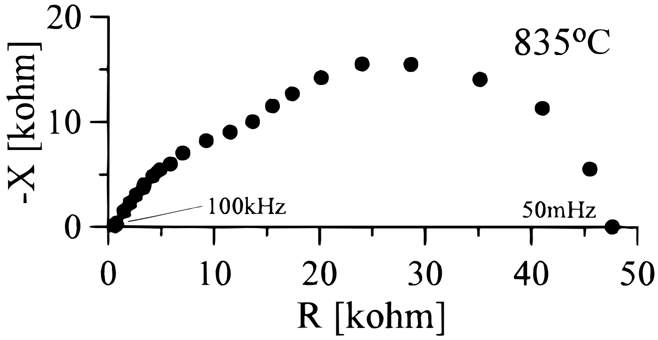

Figure 3. Impedance spectrum of a β-$Ga_2O_3/SiO_2/Al_2O_3$ sample at 835°C in dry air.

was introduced to fit the experimental data.[6] The Warburg impedance (Z_w) is a simple CPE with a phase of 45°

$$Z_w(\omega) = \frac{A}{\sqrt{\omega}}(1 - j)$$

where ω is the angular frequency, A is a fitting parameter, and $j = \sqrt{-1}$ is the imaginary unit.

In Fig. 2 the semicircle at high frequencies corresponds to the bulk resistance (R_b). However, the semicircle in the low-frequency range stands for the resistance of the space-charge region formed at the grain boundaries (R_{gb}). The ohmic character of the sample (Fig. 5) suggests that the effect of the metal/semiconductor interface in our experimental conditions cannot be detected.[7] The "height" of the semicircle at low frequencies is proportional to the capacitance of the space-charge region (C_{gb}).

The shape of the curves belonging to 835°C (Fig. 3) and 578°C (Fig. 2) is similar. However, the ratio R_b/R_{gb} increases with temperature.

Figure 6 shows the changes in the R_b and R_{gb} values as a function of temperature. They were calculated[8] from the impedance spectra of the β-$Ga_2O_3/SiO_2/Al_2O_3$ sample. As $R_{gb} > R_b$ in the entire temperature range, however, R_{gb} approaches R_b as the temperature increases. At 835°C, R_{gb} roughly equals R_b.

In Fig. 7 the R_b and R_{gb} values of the β-Ga_2O_3/BeO sample are plotted. $R_{gb} > R_b$ in the temperature range. It must be noted that this relation is valid even at high temperatures (contrary to the case of the β-$Ga_2O_3/SiO_2/Al_2O_3$ sample).

The resistance of the β-Ga_2O_3/BeO sample, in the whole temperature range, is about one order of magnitude larger than that of the β-$Ga_2O_3/SiO_2/Al_2O_3$ sample. The explanation of this phenomenon follows. In the absence of the diffusion barrier, during the heat-treatments the beryllium (and the eventual impurities of the substrate, e.g., Mg) can diffuse into the oxide semiconductor. This leads to a doping toward p-type conduction.[9]

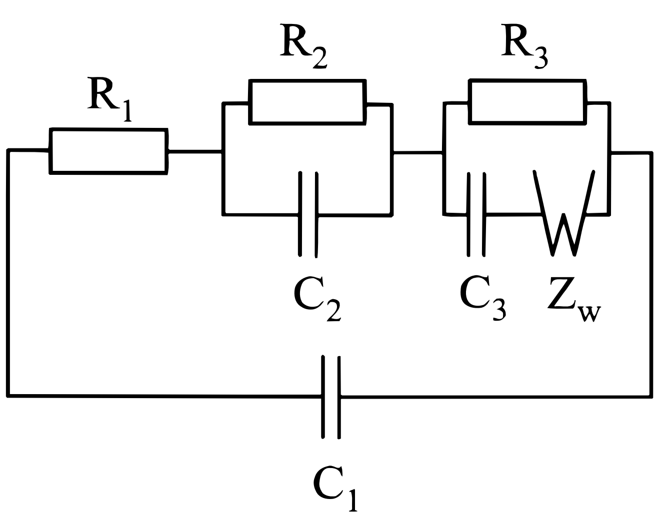

Figure 4. The equivalent circuit used for the evaluation.

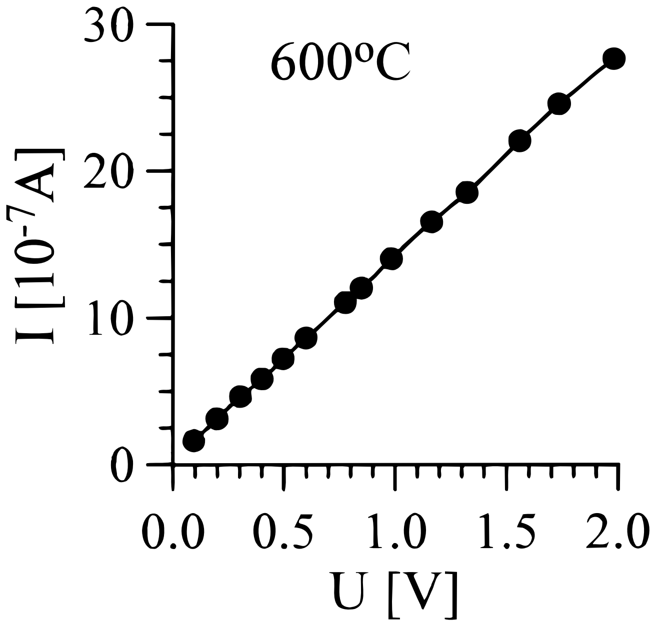

Figure 5. I-V plot of the β-$Ga_2O_3/SiO_2/Al_2O_3$ sample at 600°C in dry air.

Figure 8 shows the impedance of the β-$Ga_2O_3/SiO_2/Al_2O_3$ sample when different oxygen concentrations are applied. The results obtained by fitting the experimental data are shown in Table 1. The fitting procedure is described as follows.

An error function (H) was generated and minimized by the conjugate gradient numerical method[8]

$$H(R_1, C_1, A, R_3, C_3) = \sum_{i=1}^{n} S_i(ReZ_i - ReM_i)^2 + S_i(ImZ_i - ImM_i)^2$$

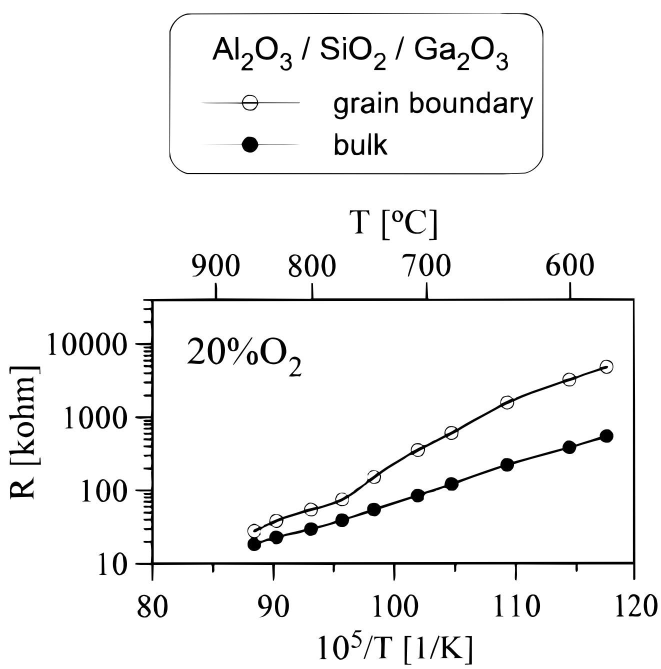

Figure 6. R_b and R_{gb} vs. $1/T$ for a β-$Ga_2O_3/SiO_2/Al_2O_3$ sample in dry air.

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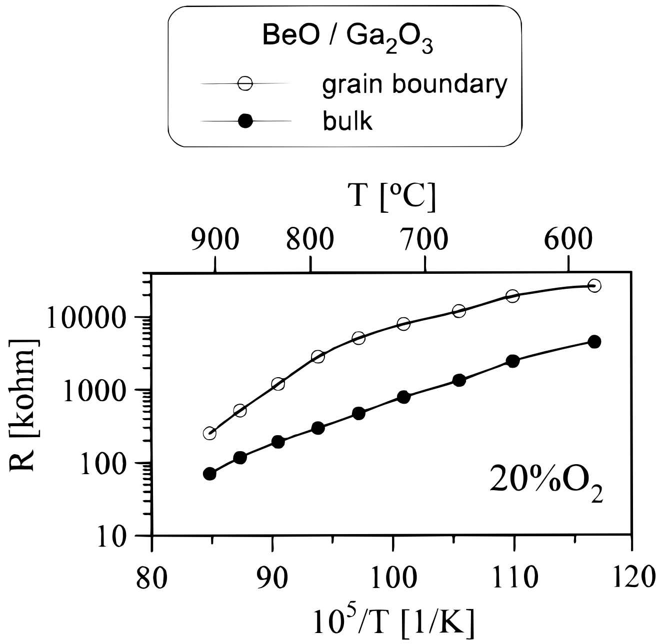

Figure 7. R_b and R_{gb} vs. $1/T$ for a β-Ga_2O_3/BeO sample in dry air.

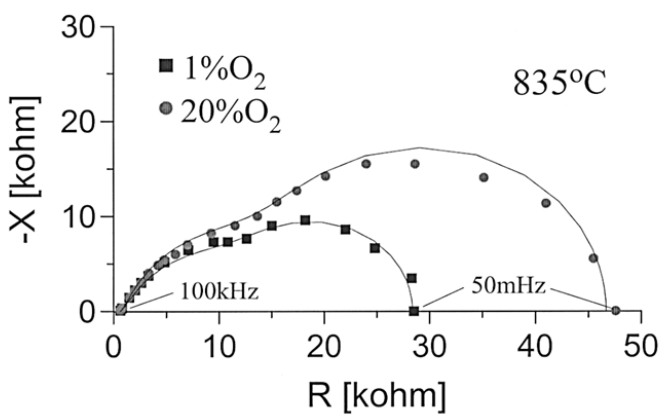

Figure 8. Impedance spectra of a β-Ga_2O_3/SiO_2/Al_2O_3 sample at 835°C in 1% and 20% O_2.

where ω_i is the angular frequency belonging to the experimental point i; Z_i the impedance at ω_i, calculated from the equivalent circuit in Fig. 4; M_i the measured impedance at ω_i; S_i the weighting factor for the experimental point i; and n is the number of the experimental points.

Table I. Bulk and grain boundary resistance values in 1 and 20% O_2, at 835°C.

	R_b (kΩ)	C_b (μF)	A	R_{gb} (kΩ)	C_{gb} (μF)
20% O_2 + N_2	15.1	0.26	5×10^4	32.0	1.3
1% O_2 + N_2	11.6	0.30	7×10^4	16.2	1.7

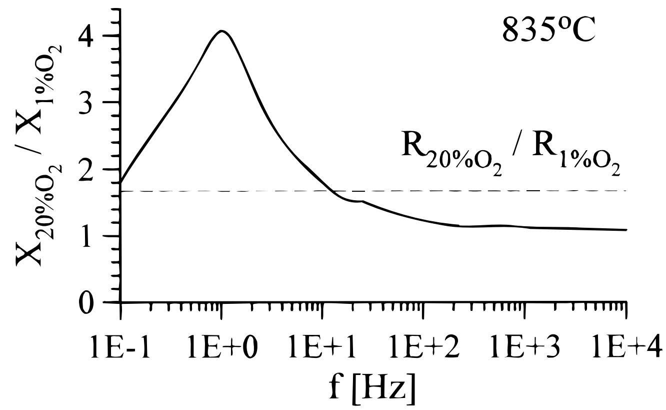

Figure 9. Frequency dependence of the oxygen sensitivity for the β-Ga_2O_3/SiO_2/Al_2O_3 sample at 835°C.

As seen in Fig. 8 and Table I, the change in the oxygen concentration from 1 to 20% affects mainly the low-frequency range of the impedance spectrum: R_{gb} increases while C_{gb} decreases. This phenomenon can be explained as follows. Oxygen is adsorbed as a negative ion on the grain boundaries,[10] giving rise to a positive space-charge region (depletion layer) in the n-type sample. This results in a resistance increase. The depletion layer broadens with the oxygen concentration, diminishing the capacity of the grain boundary. These facts suggest that the adsorption of oxygen affects mainly the grain boundaries in the polycrystalline sample.

Figure 9 shows the oxygen sensitivity vs. frequency (β-Ga_2O_3/SiO_2/Al_2O_3 sample, at 835°C). Between 100 mHz and 10 Hz the sensitivity measured by ac exceeds that measured by dc. The maximum oxygen sensitivity was found around 1 Hz; it is about 2.5 times bigger than the dc sensitivity.

Conclusions

The results of impedance measurements complete the data obtained by the dc method and offer a powerful tool to understand the conduction mechanisms. Besides this advantage they make clear that the sensitivity of a sensor for a certain gas depends on the frequency applied. Using this optimum frequency the sensor sensitivity can be seriously improved.

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