Negative admittance in resistive metal oxide gas sensors

Aapo Varpula¹, Sergey Novikov¹, Juha Sinkkonen¹, Mikko Utriainen²
¹Helsinki University of Technology, P.O. Box 3500, FIN-02015 TKK, Espoo, Finland
²Environics Oy, P.O. Box 349, 50101 Mikkeli, Finland
E-mail: aapo.varpula@hut.fi

Abstract. The negative admittance effect is observed in a WO₃-based resistive gas sensor MOS1 from Environics Oy. The effect is caused by electron trapping (i.e. oxygen ionization) at the grain boundary. The results show that the current component related to the modulation of the grain-boundary barrier dominates in dry clean air and the charging or discharging current dominates in humid air conditions. An equivalent electrical circuit model for the sensor response is presented.

1. Introduction
Resistive gas sensors are typically based on granular semiconductor materials in which electrical conduction is limited by high impedance potential barriers associated with grain boundaries [1]. Conductance is exponentially dependent on potential barrier height. This is in turn controlled by the grain boundary charge which is modulated by chemical reactions, mainly by the oxygen ionization. Barrier limited conduction provides sensitive monitoring of gas reactions.

Time-dependent phenomena in granular gas sensor materials cover a very broad time scale from nanoseconds to hours. From electrical point of view granular material is a random resistor-capacitor network, which shows frequency dispersion in admittance typically in MHz-region [2]. The oxygen ionization reaction (i.e. electron trapping) is an additional effect in sensor material, which is usually orders of magnitude slower. Impedance spectroscopy is an effective tool to study electrical properties of granular materials. In this paper we focus on low frequency regime where the electronic trapping occurs.

A structure where electrons can be trapped at grain boundaries has interesting electrical properties. Introduction of current in material injects free carriers at barrier top. This leads to increase of grain boundary charge by trapping which in turn modulates the current passing through the grain-boundary region. It turns out that this effect can be represented by a series resistor-inductor or RL electrical equivalent circuit model with negative circuit element values. Usually electron trapping can represented with a series RC electrical equivalent circuit model with positive circuit element values. However, the analysis of electron trapping at grain boundary gives a series RC circuit with negative circuit element values. This is caused by negative polarization of the grain-boundary structure due to the application of voltage.

This type of negative admittance, or negative capacitance (NC) or anomalous inductive effect has been earlier reported in various semiconductor devices and materials [3, 4, 2], e.g. organic light-emitting diodes, ZnO varistors, quantum well infrared photodetectors etc.. In SnO₂ NC
has been observed by Varghese et al. [5] and Kaur et al. [6]. Both of the groups explained the phenomenon by the movement of adsorbed ions. In this paper we show that the effect can also be explained with the barrier limited conduction and electron trapping models.

2. Model
Electrical conduction in grain-structured metal-oxide film can be calculated using the drift-diffusion theory [1, 7]. In the calculation it is assumed that the n-type semiconducting film has $N_{barr}$ serially connected identical grain boundaries and the donors are fully ionized. The grain-boundary charge density $N_B$ is related to the potential barrier height or the surface potential $V_s$ as $V_s = qN_B^2 / 2\varepsilon N_d$, where $q$ is the electron charge, $N_d$ the donor density, and $\varepsilon$ the permittivity of the material, respectively. $N_B$ is determined by the oxygen ionization reaction between the adsorbed oxygen and the free electrons, $O_{ads} + e^{-} \rightarrow \frac{k_i}{k_{-i}} O_{ads}^{-}$, which corresponds to the rate equation $dN_B/dt = k_iN_B (N_{tot}^O - N_B) - k_{-i}N_B$. Here $k_i$ and $k_{-i}$ are the forward and backward reaction rates, and $N_{tot}^O$ the total density of oxygen (assumed constant), respectively. The electron density at the grain-boundaries is given by $n_B = N_d q \exp(-qV_s/(k_BT)) \cosh\left[qU/(2k_BT N_{barr})\right]$, where $U$ is the applied voltage across the film, $k_B$ Boltzmann’s constant, and $T$ temperature, respectively. The total current can be written as

$$I_{tot} = I_B - \frac{U}{4N_{barr}V_s} \cdot Aq \cdot \frac{dN_B}{dt} + \frac{\varepsilon N_d}{N_B N_{barr}} \cdot \frac{dU}{dt}.$$

Here $I_B = I_0 \sqrt{2V_s} \exp(-qV_s/(k_BT)) \sinh\left[qU/(2k_BT N_{barr})\right]$ is the ordinary barrier limited low frequency current [7], $I_0 = A\mu(q^2N_d^2/\varepsilon^{0.5})$, $A$ the cross-sectional area of the film, and $\mu$ electron mobility respectively. The second term in Eq. (1) is arising from charging of traps and the third term from the current through the depletion layer capacitance. Linearization of $I_B$ gives the normal differential conductance and barrier modulation term with negative admittance. By linearizing Eq. (1) an electrical equivalent circuit model shown in Fig. 1a is obtained. The current through the two negative admittance circuit branches vanishes at zero bias voltage. The time constant $\tau$ of the negative admittance branches is the same. The $U$ dependence of the time constant is given by $\tau^{-1} \propto \cosh\left(qU_0/(2k_BT N_{barr})\right)$, where $U_0$ is the bias voltage. The circuit model of Fig. 1a without the capacitor $C$, whose admittance is negligible at low frequencies, can be converted into a circuit shown in Fig. 1b.

![Figure 1](image-url) (a) Electrical equivalent circuit model of the grain-boundary with a potential barrier. $C$ is the normal depletion layer capacitance and $R_{diff}$ the resistor corresponding to the differential conductance. Additionally two negative admittance branches are shown. The $R_{char}/C_{char}$ branch corresponds to the charging and discharging current and the $R_{mod}/L_{mod}$ branch to the barrier modulation. (b) Converted circuit without the capacitor $C$. The values of the elements are given by $R_{par} = R_{diff} R_{mod}/(R_{diff} + R_{mod})$, $R_b = R_{mod} R_{char}/(R_{mod} - R_{char})$, and $C_b = C_{char} (1 - R_{char}/R_{mod})$.

3. Experimental
The studied sample is commercial resistive closed-membrane-type microhotplate gas sensor MOS1 from Environics Oy developed for ChemPro®100i handheld chemical detector [10]. Details of this type of sensor are given in [11]. The grain size in the WO$_3$-based coating of the sensors is one micrometer or less. The sensor was heated to 300°C.
The admittance spectra in sub-hertz region were measured with a special measurement scheme: A Labview program varies the voltage of a Keithley 236 unit which also measures the current. The applied voltage signal consists of a constant DC bias and a uniformly distributed pseudorandom (having flat power spectral density) components. The admittance spectra were calculated from the recorded current and voltage signals by using an fast Fourier transform (FFT) algorithm with a Hanning window. The correct operation of the measurement scheme was verified by a test circuit built from commercial passive components. Clean air (0–40 % relative humidity (RH)) was produced by a humidifier and a compressed air system. The air flow through the sensor was kept at 0.2 l/min. The sensor was placed in a hermetically sealed metallic box during the measurements with humid air. In the measurements with dry air the sensor was connected directly to the air system.

![Cole-Cole plot](image1.png)

Figure 2. Admittance spectrum of MOS1 sensor in dry clean air at 300°C. The maximum of the pseudorandom voltage is 200 mV. The fit of the equivalent circuit model of Fig. 1a is shown by the black solid line.

![Cole-Cole plot](image2.png)

Figure 3. Admittance spectra of MOS1 sensor at various bias voltages in clean humid air (30–40 %RH) at 300°C. The data with 0.00–1.00 V bias were measured with maximum pseudorandom voltage of 50 mV, and the others with 200 mV. The fits of the equivalent circuit model of Fig. 1b are shown by black solid lines. The values of the circuit elements are shown in Fig. 4.

4. Results and discussion
The proposed model, Eq. (1) and Fig. 1a, fits well in the admittance spectrum measured in dry air shown in Fig. 2. The humid air (30–40 %RH) data at various bias voltages are shown in Fig. 3. The equivalent circuit shown in Fig. 1b is fitted in the data. Both $R_b$ and $C_b$ are negative as shown in Fig. 4. Furthermore, the DC-bias dependence of $R_b$, $C_b$, and the time constant is in accordance with Eq. (1). Similar results as in Fig. 3 were also obtained in the
measurements performed at higher frequencies (5 Hz – 1 kHz) with a HP4192A impedance analyzer and SnO₂-based sensor MOS3 from Environics Oy.

Figs. 2 and 3 the real part of the admittance is positive which indicates that it is dominated by $R_{\text{dif}}$. In dry air, Fig. 2, the imaginary part of admittance is positive, whereas in humid air, Fig. 3, it is negative. This indicates that the barrier modulation $R_{\text{mod}}$–$L_{\text{mod}}$ branch dominates in dry air and the charging branch in humid air conditions.

In order to explain the spectra measured in humid air, the proposed model, Eq. (1), should have an extraordinary high charging and discharging term. This suggests that the trapping takes place in a much larger area than the path of the current or indicating ion movement along the grain boundaries. However, the bias voltage dependence of the values of the circuit elements and the time constant is in agreement with the proposed model, Eq. (1). In [5, 6] the negative admittance effect was explained by the movement of ions alone. However, the proposed model and our results suggest that the main causes of the negative admittance effect are the barrier modulation and the polarization properties of the grain-boundary region and the ions provide enhancement of the charging and discharging component only.

5. Conclusions

The negative admittance effect was observed in a WO₃-based resistive gas sensor MOS1 from Environics Oy. The effect is caused by electron trapping at the grain boundary. The results show that the current component related to the modulation of the grain-boundary barrier dominates in dry clean air and the charging or discharging current dominates in humid air. The sensor response in dry clean air can be explained by the proposed model, but ion motion is needed in order to explain the strong charging current in humid air. However the bias voltage dependence of the admittance is in agreement with the proposed model.

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References
[1] Barsan N and Weimar U 2001 J. Electroceramics 7 143–67
[2] Greuter F, Blatter G 1990 Semicond. Sci. Technol. 5 111–37
[3] Ershov M, Liu H C, Li L, Buchanan M, Wasilewski Z R and Jonscher A K 1998 IEEE Trans. Elec. Dev. 45 10 2196–206
[4] Pingree L S C, Scott B J, Russell M T, Marks T J and Hersam M C 2005 Appl. Phys. Lett. 86 073509
[5] Varghese O K and Malhotra L K 2000 J. Appl. Phys. 87 10 7457–65
[6] Kaur M, Gupta S K, Saxena V, Katti V R, Gadkari S C and Yakhmi J V 2005 Sens. Actuators 107 360–5
[7] Sinkkonen J 1980 Phys. Stat. Sol. (b) 102 621–7
[8] Fort A, Rocchi S, Serrano-Santos M B, Spinicci R and Vignoli V 2006 IEEE Trans. Instr. Meas. 55 6 2102–6
[9] Ionescu R, Llobet E, Al-Khalifa S, Gardner J W, Vilanova X, Brezmes J and Correig X 2003 Sens. Actuators B 95 203–11
[10] Environics Oy http://www.environics.fi/
[11] Simon I, Barsan N, Bauer M and Weimar U 2001 Sens. Actuators B 73 1–26