



*Dedicated to the memory of
Professor Eugen Segal (1933-2013)*

GRAIN BOUNDARY CONTROLLED ELECTRON TRANSFER IN OXIDE/GAS SYSTEM

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The electron transfer between grains-boundaries in oxide/gas system can be explained using the thermionic emission. The obtained kinetic law which is a logarithmic one has been discussed.

$$I = \frac{V_1 - V_2 \ln(t + t_0)}{R}$$

INTRODUCTION

The microscopic study of charge transfer processes in oxide/gas systems is of central importance to understand the electrical conductivity changes in surface reactions and gas sensors.¹⁻⁴ During the formation of the materials, grains may be formed and therefore contribute significantly to the electrical conduction of the material.

The oxide grains are connected to each other by grain boundaries or by necks. When the grains are connected to their neighbors through grain-boundaries, a potential barrier for the migration of electrons is formed across each grain-boundary. It is the Schottky barrier.⁵⁻⁷ This barrier has a dominant role in determining the electrical resistance of the semiconductors.

In the present paper we aim at studying the influence of an applied voltage across the grains boundary.

THE MODEL

For simplicity it was assumed that the dimensions of oxide grains (n-type

semiconductors) are much larger than the Debye length, which allows to the approximation of a depletion layer of each grain by a one dimensional model.

Let a polycrystalline oxide be its grain-boundary barrier being represented by the energy-band diagram (Fig. 1).

Assuming that the conduction is mainly due to thermionic emission^{1,6} the current I across a grain-boundary is:

$$I = \frac{en}{D} \left(\frac{kT}{2\pi m} \right)^{1/2} \exp\left(-\frac{eV_s}{kT}\right) \left[\exp\left(\frac{eV_a}{kT}\right) - 1 \right] \quad (1)$$

where n is the free electron density in the grain body, m the effective mass of an electron, V_s the grain-boundary barrier height, V_a the supplementary voltage applied across the grain-boundary, e the charge of an electron, D the grain size, k and T having their usual meanings.

At high voltage

$$\exp\left(\frac{eV_a}{kT}\right) \gg 1 \quad (2)$$

and the current which passes the grain boundary becomes:

$$I = I_0 \exp\left(\frac{eV_a}{kT}\right) \quad (3)$$

where I_0 is:

$$I_0 = \frac{en}{D} \left(\frac{kT}{2\pi m}\right)^{1/2} \exp\left(-\frac{eV_s}{kT}\right) \quad (4)$$

On the surface grains exists a charge Q and the diminution of this charge in time due to the appearance of the current is:

$$\frac{dQ}{dt} = -I \quad (5)$$

But the surface charge is also:

$$Q = \varepsilon \left| \vec{E} \right|_{x=0} = \varepsilon \frac{V_a}{D} \quad (6)$$

where E is the electric field and $x=0$ means at the surface. The applied voltage V_a is approximately equal to the electric field E across the grains boundary,¹ multiplied by the grain size D , ε being the dielectric constant.

From equations (3), (5) and (6) it results:

$$\frac{dQ}{dt} = \frac{\varepsilon}{D} \frac{dV_a}{dt} = -I = -I_0 \exp\left(\frac{eV_a}{kT}\right) \quad (7)$$

From equation (7) one obtains finally:

$$-\frac{dV_a}{dt} = \frac{D}{\varepsilon} I_0 \exp\left(\frac{eV_a}{kT}\right) \quad (8)$$

which is nothing else than the differential form of typical logarithmic law. By integration one obtains:

$$V_a = V_1 - V_2 \ln(t + t_0) \quad (9)$$

$$V_1 \text{ being } \frac{kT}{e} \ln\left(\frac{I_0 e}{kT \varepsilon}\right)$$

Taking into account that:

$$I = V/R \quad (10)$$

where R is the grain boundary resistance, it results:

$$I = \frac{V_1 - V_2 \ln(t + t_0)}{R} \quad (11)$$

The decrease of the current in time, due to the applied voltage obeys a logarithmic law.

Equation (9) presents some problems in its analytical application. When $t \rightarrow \infty$ $V_a \rightarrow -\infty$ and if $t_0 \leq t$ then $V_a \rightarrow -\infty$ also for $t \rightarrow \infty$.

Logarithmic laws like equation (9) were obtained several times⁸⁻¹³ in case of gas desorption from solid surfaces. Also equation like (9) or (11) could be applied in sensor operations using large grains size,¹ because in this case the grain-boundary resistance becomes dominant. When the grains are connected only by grain boundaries, the grain-size effect on sensitivity¹ does not exist, this effect becomes relevant for oxides with small grain sizes where the neck mechanism becomes important.

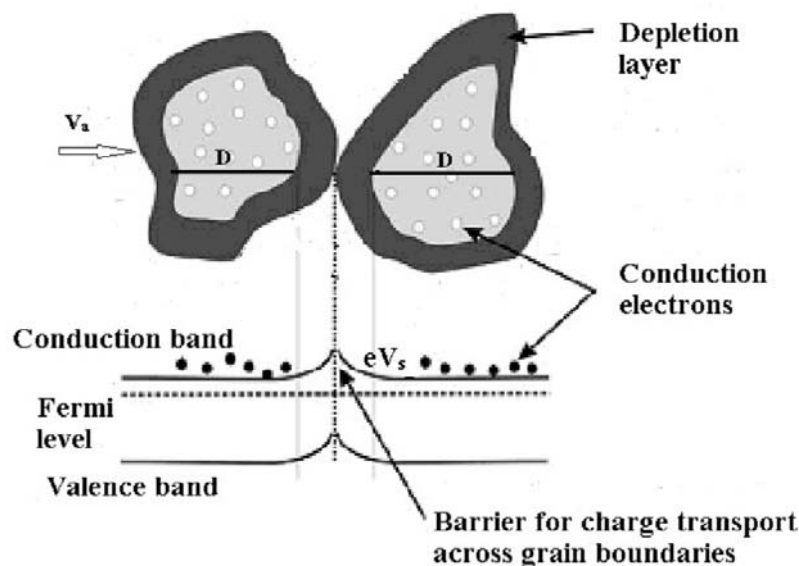


Fig. 1 – Grain-boundary connection and energy – band diagram of a n-type oxide semiconductor.

CONCLUSIONS

The electron transfer between grains-boundary in oxide-gas systems can be explained using thermionic emission. The obtained kinetic law is a logarithmic one similar with the law of gas desorption from an oxide surface.

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REFERENCES

1. X. Wang, S.S. Yee and W. P. Carey, *Sensors Actuators B*, **1995**, 24-25, 454.
2. N. Bârsan and U. Weimar, *J. Electroceramics*, **2002**, 7, 143.
3. N. Yamazoe and K. Shimano, *Sensors Actuators B*, **2008**, 128, 566.
4. S. M. Sze, "Physics of semiconductors devices", Wiley, New-York, 1981, p. 255.
5. K. Hauffe and S. R. Morrison, "Adsorption", de Gruyter, Berlin, 1979, p.87.
6. S. R. Morrison, "The Chemical Physics of Surfaces", Plenum Press. New-York and London, 1990, p. 263, 276.
7. S. R. Morrison, *Sensors Actuators*, **1987**, 11, 283.
8. N. I. Ionescu, *Bulg. Chem. Commun*, **1992**, 25, 39.
9. N. I. Ionescu, *Rev. Roum. Chim.*, **1992**, 37, 509.
10. N. I. Ionescu and M. Caldararu, *Rev. Roum. Chim.*, **2006**, 51, 521.
11. N. I. Ionescu and M. Caldararu, *Rev. Roum., Chim.*, **2008**, 53, 603.
12. N. I. Ionescu, *Rev. Roum. Chim.*, **2008**, 53, 535.
13. N. I. Ionescu, *Rev. Roum. Chim.*, **2011**, 56, 483.

