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Conduction mechanisms in SnO_2 single-nanowire gas sensors: An impedance spectroscopy study

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ABSTRACT

Results of studies on single and multiple SnO_2 nanowire gas sensors with impedance spectroscopy are reported. Equivalent circuit modeling is used to draw fundamental conclusions about the dominant conduction mechanism in single-nanowire sensors, where the diameter of the nanowire is found to play a key role. This is then extended to multiple-nanowire sensors. For single-nanowire sensors, I–V measurements are also used to demonstrate that the contribution from the electrode-nanowire contact to the overall resistance changes with atmosphere and temperature. We find that for the randomly-orientated multiple-nanowire sensors, the main contribution to the resistance comes from the nanowire–nanowire junction.

1. Introduction

There is an increasing need for low-cost, low-power and highly sensitive gas sensors for commercial and industrial applications in health and safety areas such as hazardous gas monitoring, medical diagnosis, emission control in combustion processes and many other. Over the last few decades, resistive-type polycrystalline oxides have been used in gas sensors due to simple and low-cost fabrication, but their sensitivity, selectivity and response time need further improvements [1–5]. Nanostructures are meeting these needs with a higher surface-to-volume ratio that increases the interaction between the gas species and the surface. These structures are extensively studied and there are many synthesis routes to obtain those [6,7]. Commercial production of crystalline nanowires is becoming affordable and reproducible at industrial scales [8]. Many researchers design gas sensors based on these nanowires that are highly sensitive and selective to different gases, but the general approach to improve these devices is a trial-and-error method. Impedance spectroscopy is a novel approach to understand these materials and guide design of new nanostructures, as highlighted by a recent review [41]. It gives the same information as the usual DC measurements that the vast majority of researchers use, but also yields fundamental information about the physicochemical processes that govern the electrical response, such as electrode interface contributions, bulk and surface reaction with different gases [9–12].

In this work, single-nanowire and multiple-nanowire SnO_2 gas sensors were tested toward different gases and temperature conditions with the goal of understanding the conduction mechanism that governs the electrical response. Single-nanowire and multiple-nanowire sensors were measured using I–V curves along with impedance spectroscopy measurements to quantify the Pt electrode-nanowire contact and the intrinsic nanowire contribution separately. An equivalent circuit model that reflects these data was then proposed to explain the conduction mechanism as a function of nanowire diameter, operating temperature, and atmospheric oxygen content.

2. Conduction mechanisms

A Schottky barrier is a potential energy barrier that is typically present at metal-semiconductor junctions, induced by dissimilar work functions or electron affinities of two materials in electrical contact. This type of energy barrier can be found at any interface including surfaces in which a semiconductor is involved. A Schottky barrier can be characterized by two parameters: height (in energy) and width (in distance). In an n-type semiconductor, oxidizing atmospheres like oxygen have the tendency to increase the

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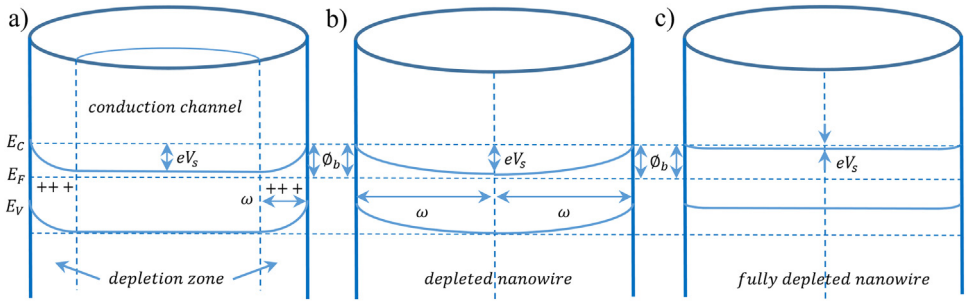

Fig. 1. Band gap diagram in nanowires. (a) A nanowire with a depletion zone at the surface and with free carriers in its center where conductivity is high. This is the depletion width established by surface processes. (b) Due to oxygen in-diffusion, the nanowire center becomes partially depleted. The band bending is the same as in the previous case. The conduction channel width reduces to zero and the conduction through the nanowire decreases significantly. The conduction between the nanowires is also reduced from decreased tunneling. (c) If oxygen in-diffusion continues, it leads to the lifting of the conduction band from E_F and the band bending becomes smaller than ϕ_b. The barrier height remains constant in the whole diffusion process as long as the temperature and atmosphere are kept constant. It is important to point out that when barriers are not overlapped, $\phi_b \approx eV_s$ is regularly considered as a good approximation.

barrier height due to charge accumulation at the interface caused by chemisorbed oxygen bonding with free electrons. This causes a local increase of the electric field which increases the potential, with a maximum at the interface. This barrier can be seen as upward-sloping conduction and valence band edges in Fig. 1. Inert gases such as nitrogen only modify the oxygen coverage of the surface by creating a lower equilibrium oxygen concentration. Barrier width is established by a charge equilibrium between the negatively-charged interface and the compensating positively-charged region depleted of mobile carriers, called the depletion layer.

Electrical properties of oxide semiconductors are usually described by a one-dimensional model representing the interface between two particles. It is also regularly considered that a thermionic (thermally-activated) mechanism is responsible for the sample conductivity and is described by

$$J_{thermionic} = AT^2 e^{-\phi_b/kT}, \tag{1}$$

where $\boldsymbol{\phi_b}$ is the barrier height and is defined as the band bending plus the difference between the conduction band minimum (CBM) and the Fermi level $\phi_b = eV_s + (E_{CBM} - E_F)$ (see Fig. 1). J, T, k and A are current density, the absolute temperature, the Boltzmann constant and the Richardson constant [13], respectively. This equation reflects an activated process due to inter-particle barriers.

Further, it has been pointed out in previous works of the group [14–17] and other researchers [18,19] that an additional tunneling contribution is unavoidable for the usual barrier characteristics and can be calculated as

$$J_{tunneling} = \frac{AT}{k}\int_0^{Vs} F(E) * P(E)\, dE, \tag{2}$$

where $F(E)$ is the Fermi-Dirac distribution function and $P(E)$ is the transmission probability determined by the one-dimensional and time-independent Wentzel-Kramers-Brillouin (WKB) approximation. After integration and for a parabolic barrier, P(E) can be expressed as in Ref. [18]. The total conduction in the sample can be calculated as the sum of both contributions: thermionic and tunneling. *Thus, the thermionic conduction mechanism only depends on barrier height and the tunneling mechanism depends both on barrier height and width.* Eq. (1) indicates that only carriers with energy higher than the barrier contribute to the conduction. Similarly, Eq. (2) accounts for carriers with energies between the CBM and the top of the barrier that contribute to conduction through tunneling. For these kinds of metal oxides, both contributions can be relevant. Tunneling becomes the dominant conduction mechanism as temperature decreases and/or doping increases. [18,19].

When oxygen chemisorbs on the nanowire surface, equilibrium is quickly reached. As stated above, this increases the barrier height [20]

$$\frac{1}{2}O_2(g) + S \leftrightarrow O^0_{ads} \tag{3}$$

$$O^0_{ads} + e^- \leftrightarrow O^-_{ads}, \tag{4}$$

where S corresponds to an adsorption site on the surface and (g) refers to a gas phase. This implies that more ambient oxygen increases chemisorbed oxygen and induces a larger barrier height. Assuming a constant temperature, this process continues until the surface of the material reaches an equilibrium of adsorbed oxygen.

It is considered, as an approximation, that defect states within the band gap above the Fermi level, E_F are empty and below are full. Oxygen chemisorbing on the surface traps conduction electrons at energies that lie within the band gap. This reduction of charge carriers causes the conduction band to bend upwards, away from the Fermi level. Thus, a depletion region of width ω is formed, where electron density is very low [16,21,22].

In SnO_2, oxygen vacancies are the dominant defects and behave as donor impurities with densityN_d. The oxygen exchange equilibrium is regularly written as

$$O^-_{ads} + e^- \leftrightarrow O^{2-}_{int} + S \tag{5}$$

$$V^{2+}_O + O^{2-}_{int} \leftrightarrow O_{latt} \tag{6}$$

There are several steps in these equations: a possible mechanism is that neutral oxygen in the crystal O_{latt} leaves its site to create a doubly ionized vacancy V^{2+}_O and a doubly ionized interstitial O^{2-}_{int}. Then, the oxygen interstitial migrates to the surface and finally becomes neutral to desorb into the gas phase. Eqs. (3)–(6) describe the mechanisms in which oxygen goes from the bulk to the gas phase and vice versa: oxygen adsorption (Eq. (3)), surface ionization (Eq. (4)), bulk incorporation as an ion (Eq. (5)) and finally vacancy annihilation (Eq. (6)).

By adding Eqs. (3)–(6) we obtain

$$V^{+2}_O + 2e^- + \frac{1}{2}O_2 \leftrightarrow O_{latt} \tag{7}$$

and the corresponding mass action law for Eq. (7) is [23]

$$K = \left[V^{2+}_O\right]\left[e^-\right]^2 p(O_2)^{1/2} \tag{8}$$

Square brackets denote concentration and K is the mass action constant or the equilibrium constant. Eq. (8) indicates that, at equilibrium, the oxygen vacancy concentration directly depends on the oxygen partial pressure in the gas phase. Previous studies by this group [14] have shown that the equilibrium barrier height depends