Extended Abstract

Work Function Measurements in Single-Crystalline In₂O₃ for Conduction Modelling [†]

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To date, there are only a few studies on the gas sensing properties of single crystalline sensors. The preferred study of polycrystalline materials is mainly due to the considerably larger sensor signals, which are caused by the presence of grain boundaries [1,2]. However, the high quality and controlled growth of single-crystalline materials has the promise to help the fundamental understanding of sensing: the electrical measurements of crystals under in- operando temperatures and different gas atmospheres are an avenue for directly extracting fundamental electronic behaviour of each material that is essential for building an accurate model of sensor behaviour. Due to the recent advance in the development of in-operando investigation methods, it seems now possible to combine them with controlled single crystalline model sample.

Indium oxide is a wide-bandgap semiconducting material with a direct bandgap of around 2.8–2.9 eV. It has been extensively used as a transparent conductive oxide (TCO) in electronics, for photovoltaic devices, light emitting diodes and chemical sensors [3,4]. Nevertheless, the knowledge about sensing with In₂O₃ based devices is still insufficient.

Here, we present results of investigations performed on an approximately 440 nm thick crystalline In₂O₃ film grown by plasma-assisted molecular beam epitaxy (PA-MBE) on a YSZ substrate. Combined DC resistance and work function change measurements performed at an operation temperature of 300 °C in various atmospheres were used in order to obtain information about the conduction mechanisms and electronic properties of the material in the same manner that was previously employed for the study of polycrystalline samples [5].

The work function and resistance changes are measured with the Kelvin Probe technique, which is a non-contact, non-destructive method that uses a vibrating reference electrode and measures the changes of the contact potential difference (CPD) between the sample and the electrode. Variations in the CPD induced by changes in the gas atmosphere represent relative work function variations of the sample [2]. The work function in a semiconductor can be expressed by

$$\varphi = \chi + (E_C - E_F) + V_S, \tag{1}$$

where V_s is the surface band bending, χ represents the electron affinity, which we assume constant when no humidity is present, and $(E_C - E_F)$ is the difference between the conduction band in the bulk and the Fermi level.

In Figure 1 the dependence of the sample conductance on work function changes is presented. Experimental results will be interpreted using two approaches. First, all changes will be attributed to V_s (surface processes), meaning that no bulk electron concentration changes are allowed in the model. Next, all changes will be attributed to bulk-related processes, where only the bulk electron concentration changes $(E_C - E_F)$ and no band bending at the surface is present.
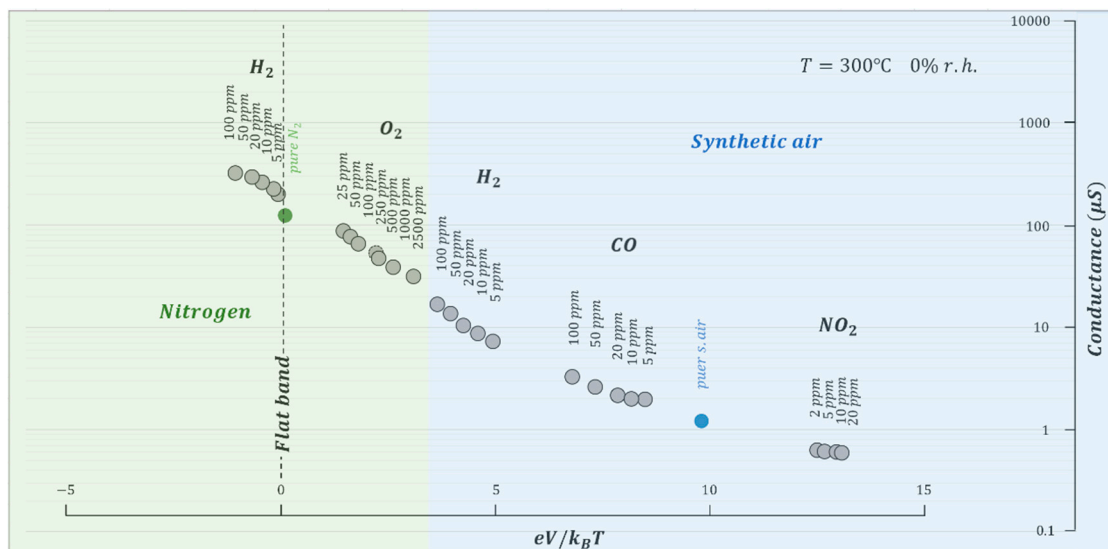

Figure 1. Conductivity against relative work function changes measured at 300 °C with no humidity present. The φ measured in nitrogen is taken as the flat band condition. The green and blue area represent the carrier gas present.

The total conductance of a compact layer is the sum of the part of the layer influenced by surface processes and the conductance of the layer that is left unchanged, the bulk.

$$G_{total} = G_s + G_b = \frac{e\mu W}{L} [Z_0 n_s + (D - Z_0)n_b] \tag{2}$$

In Equation (2), L is the length of the layer, W its width, D its thickness and Z_0 the thickness of the surface layer and μ the mobility.

Room temperature experiments indicate that a large downwards band bending is present, which is causing the appearance of a surface electron accumulation layer (SEAL) [6] that cannot be described using Boltzmann statistic. For that reason, a numerical conduction model using Fermi-Dirac statistics, which are valid for all electron densities, has been developed. This was solved with an iterative process to find equilibrium concentration of electrons in the bulk (n_b) and surface properties such as band bending and surface density of electrons (n_s). The fitting parameters (fitting not shown here) would imply a bulk electron concentration of $n_b = 5.6 \times 10^{19}$ m^{-3}, which would be very low and not realistic.

On the other hand, if we apply a flat band approach, where all changes in conductivity and work function are due to variations of $(E_C - E_F)$, the results also cannot be fully explained. From the experimentally measured conductance in pure nitrogen and pure synthetic air (green and blue points in Figure 1), the bulk electron concentration found is $n_b = 4.7 \times 10^{23}$ m^{-3} and $n_b = 4.7 \times 10^{21}$ m^{-3} respectively. From this, the difference between the Fermi Level and the conduction band can be estimated, using the effective density of states $N_C = 5.9 \times 10^{24}$ m^{-3} and Equation (3):

$$(E_C - E_F) = (\frac{k_B T}{e}) \ln[\frac{N_C}{n_b}] \tag{3}$$

Here, this difference is $(E_C - E_F) = 0.125$ eV in pure nitrogen and $(E_C - E_F) = 0.350$ eV in synthetic air. These results indicate that the experimental changes in conductance (a factor 100 from

nitrogen to synthetic air) and work function differences (approximately 0.5 eV) are neither purely due to bulk changes nor purely surface dominated and implies that the atmosphere changes affect both bulk and surface electron concentration.

References

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