OXYGEN CHEMISORBED STATES AND ITS ELECTRONIC LEVELS ON (111) In_2O_3 SURFACE: PHOTOEMISSION AND PHOTOCONDUCTIVITY STUDIES.

V.Brinzari[1], M.Ivanov[1], G.Korotcenkov[1], M.Kamei[2]

[1]Lab. of Micro- and Optoelectronics, Technical University of Moldova,
Bld. Stefan cel Mare, 168, Chisinau, 2004, Moldova. E-mail: vbrinzari@yahoo.com
[2]National Institute for Material Science, Namiki, Tsukuba, Ibaraki, Japan

The fundamentals of gas response mechanism of metal oxide conductometric sensors and in particularly for the In_2O_3-based ones as far remain in dispute. The difficulties in description of operation mechanism and the problems in this area are determined first of all by the lack of essential information concerning surface electronic levels modulated by environment (mainly by oxygen), which are responsible for surface conductivity changes. So far it is not clear what is the nature of oxygen induced levels – is it redox (due to changes in a surface stoichiometry) or adsorptive? Where they are positioned in a band gap of semiconductor and what is their dispersion? What are activation energies of their formation? As before this principal and starting point for any gas sensor model is characterized by rather speculative approaches and a lack of any experimentally confirmed facts.

Here we present results provided by two different experimental methods on direct observations of such surface states originated from oxygen containing species adsorbed on In_2O_3. They are: synchrotron radiation photoemission spectroscopy (SRPES) and photoconductivity spectroscopy (PCS). During the cycle of photoemission experiments for a valence band (VB) and band gap (BG) regions on (100) and (111) epitaxial layers of In_2O_3 on YSZ single crystal substrates aimed on elucidation of reduction-oxidation properties of these surfaces, it were found the oxygen induced states located at~0.2 eV below Fermi level (~0.5-0.6 eV below CB). Photoemission peak corresponding to them demonstrates opposite behavior (increases) to exposure of oxygen (~100L) if to compare with so-called defect states that decrease in intensity with oxygen dose. This peak is thermally activated and reaches a maximum value at T~250° C. It was revealed on (111) surface only. Measured samples were of good crystallinity that was checked by LEED, RHEED, XPD and AFM methods. During these experiments it was also obtained the information concerning the position of VB maximum under various surface treatments in UHV conditions (annealing, Ar-sputtering, exposures of O_2, CO, H_2O at different temperatures), which allowed estimating the changes of surface potential. It was found the abnormal reactivity behavior of (111) surface to CO dose at T~150-250°C which in agreement with our earlier revealed acceptor-like CO response of In_2O_3 film conductivity.

Other cycle of experiments was done on epitaxial and nanocrystalline films (deposited by spray pyrolysis, thickness ~30nm) using photoconductivity measurements. Due to some growth features nanocrystallites possessed a preferential (111) faceting. Photoconductivity was measured in the spectral range of 0.26-0.5μm at various temperatures in reducing and oxidizing atmospheres (1%H_2, ~1ppm O_3). Wide peak distinguished at long-wave part of photoresponse tail was found near 0.43 μm under O_3 treatment at T~250°C. It behavior was fully reversible. In reducing atmosphere the spectral photoresponse increases near the fundamental absorption edge (FAE) and decreases for the above-mentioned region comparing to common air. We subscribed the peak at 0.43 μm to oxygen induced surface states positioned at 0.4-0.6 eV below CB. Evidently, it is in agreement with SRPES results. The changes of photoresponse near FAE are probably due to defect states. We did not find such peak on (100) In_2O_3 films. Transient behavior under/after illumination of photoresponse in air, transient behavior in ozone and in switching cycle air/N_2 allowed to make a conclusion that other processes than electron transitions between oxygen induced states and CB determine the temporal behavior of thin film gas response. In case of thin nano-crystalline films photoconductivity properties drastically differ from their bulk ones. The contribution from surface being as a trapping and recombination region for excited charge carriers becomes dominant. In turn there is a dramatic impact on charge carrier transfer due to intergrain contacts. The role of adsorbed oxygen as acceptor-like states consists in recombination with photogenerated holes with consequent desorption of oxygen species. Such surface discharging results in an increase of electron concentration, thus electrons, which are major charge carriers, determine the monopolar type of photoconductivity. Finally the comparison with SnO_2 photoconductivity response is illustrated and principal differences are discussed.

This work had financial support from CRDF-MRDA in the frame of US-Moldova bilateral agreement, and ICTP in the frame of grant 2004500.