MODELING OF ATMOSPHERE SENSITIVE HETEROJUNCTIONS FOR DEVICE APPLICATIONS

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Simple and inexpensive methods of detecting pollutants in ambients are needed for maintenance of safe environment in modern industries. Chemical sensors based on catalytic combustion and using solid state electrolytes and semiconducting oxides etc. are being developed for this purpose. Sensors based on semiconducting oxide utilise the resistivity change in oxide semiconductor material when they are exposed to pollutants. Heterojunctions are known to be atmosphere sensitive, and they are also incorporated in there sensors to increase their sensitivities. Electrical properties of heterjunctions such as CuO-SnO_2, CuO-ZnO, NiO-ZnO and NiO-SnO_2, and their dependence on composition of ambient gas phase have been studied experimentally [1-3], mainly by carrying out I-V and C-V characteristics of junctions to achieved between individual pellets by spring loading them. Band energy diagrams corresponding to these junctions would be needed to understand their properties and these are not available. In the paper, synthesised band energy diagrams of these heterojunctions are purposed based on reported experimental data.

Schematics of the band diagram of a p-n junction, e.g for CuO-SnO_2 is shown in figure 1. The energy difference between the Fermi level and the valence band (p-type), δp, or the conduction band edge (n-type) ,δn, for each oxide is obtained from their carrier densities [4]:

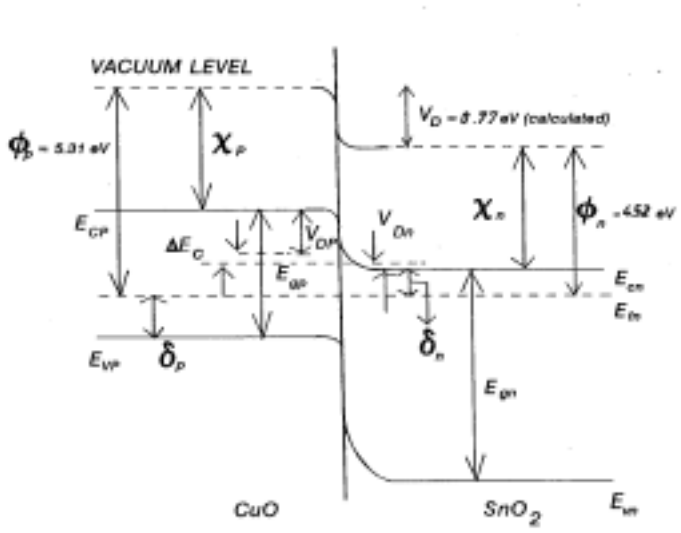
$$p = 2(2\pi m^* kT/ h^2)^{3/2} \exp (\delta p/ kT) \qquad (1)$$

$$n = 2(2\pi m^* kT/ h^2)^{3/2} \exp (\delta n/ kT) \qquad (2)$$

where m^* is the effective mass, k is the Boltzmann constant, T is the temperature and h is the Planck's constant. Table 1 lists the literature data on the carrier concentrations, electron affinity,χ, band gap energy, Eg ,and the workfunction, φ, of the CuO[5], SnO_2[6], ZnO[7-8] and NiO[9]. The δp and δn values deduced from the above equations are listed in Table 1.

The electronic behavior of an heterojunction is similar to that of a homojunction except for new boundary conditions which cause jumps of band edges at the interface. These jumps originate from the band offsets, effective mass, carrier mobility and the dielectric constant discontinuities. A rectifying barrier is formed at these p-n

heterojunctions due to the existence of charge depletion region, as found experimentally for the NiO-ZnO [3], CuO-ZnO [2].



E_c: Lower level of conductiin band
E_F: Fermi-level
E_V : Upper level of valence band
V_D: Diffusion potential
ΔE_c: conduction band discontinuity
φ : Work function
δ: Energy difference between Fermi level and conduction /valence band edge

Fig.1 Synthesized energy band diagrams of CuO-SnO_2

TABLE 1 : Data on bulk properties of oxides

Semiconduc-ting Oxide	Carrier conc. (cm^{-3})	Electron affinity, χ (eV)	Energy gap Eg(eV)	Work Function φ (eV)	δn (eV)	δp(eV)
CuO	$2.1x10^{17}$	4.07	1.35	5.3		0.12
SnO_2	$5x10^{16}$	4.49	3.8	4.525	0.034	
ZnO	$4x10^{16}$	4.2	3.3	4.25	0.05	
NiO	$1.3x10^{19}$	1.4	3.47	4.77		0.07

Under equilibrium conditions when no bias voltage is applied, depletion widths at n- and p- type sides, L_n and L_p respectively, can be represented as follows:

$$L_n = [2p\varepsilon_n\varepsilon_p V_D/\{en(n\varepsilon_n + p\varepsilon_p)\}]^{1/2} \qquad (3)$$

$$L_p = [2n\varepsilon_n\varepsilon_p V_D/\{ep(n\varepsilon_n + p\varepsilon_p)\}]^{1/2} \qquad (4)$$

where V_D is built-in potential or contact potential which is also called as diffusion potential, ε_n and ε_p are dielectric constants of n- and p- materials. The height of built-in

potential can vary from nearly zero (high T) to about band gap energy (low T). In the absence of any experimental data, the maximum possible value of V_D can be obtained by taking an average of band gap energies of two materials. This value can also be obtained from the difference between the experimentally determined fermi level energies or work functions of the materials.

Experimentally, one can also derive V_D values by measuring capacitance, C at various bias voltages (C-V plot) for a given junction. At low bias voltages, $1/C^2$ varies linearly with bias volatage, as given by the following relation [7,8]:

$$1/C^2 = (V_D-V)/[qnp\ \varepsilon_n\varepsilon_p /2(\varepsilon_n n+ \varepsilon_p p)] \qquad (5)$$

From the x-axis intercept of a plot of $1/C^2$ vs bias voltage, V_D can be obtained. In the case of CuO-ZnO heterojunction, for obtaining V_D, the C values for various bias voltages are taken from Fig. 3 of ref [2]. From a linear fit of this data as per equation (5) the V_D for this junction is obtained as 1.09 eV (Table 2). Since detailed studies on C vs Bias voltage behaviour have not been made for CuO-SnO_2, NiO-SnO_2 and NiO-ZnO junctions, diffusion potentials were obtained, using their respective work function data, as below and are listed in Table 2:

$$V_D = (\varphi_p-\varphi_n) \qquad (6)$$

Using this V_D value, the conduction band edge discontinuity ΔE_c for each junction is determined from the relation:

$$\Delta E_c = E_{gp}-V_D - \delta p - \delta n \qquad (7)$$

where E_{gp} is the energy gap of the p-type semiconductor. The ΔE_c values thus calculated are presented in Table 2.

TABLE 2 Calculated values of ΔE_c and V_D for various heterojunctions

Heterojunction	ΔE_c (eV)	V_D (eV)
CuO-SnO_2	0.42	0.77
CuO-ZnO	0.35	1.09
NiO-SnO_2	3.1	0.275
NiO-ZnO	2.83	0.52

Depletion widths, L_p and L_n are calculated from equations (4) and (5). Table 3. shows the values of L_p, L_n and L_T ($= L_n + L_p$) for different heterojunctions considered in this work. Since $L_n >> L_p$, the depletion effect on the electrical properties will be significant in ZnO

or SnO_2 matrix with CuO or NiO as inclusion and forming the junctions. The effect will be less pronounced when the p-type oxide is the matrix. Carrier concentration n and diffusion potential V_D are strongly dependent on temperature and adsorbates such as oxygen and hence depletion layer widths will be determined by these parameters. A decrease in temperature leads to a decrease in n and thus results in an increase in depletion layer width (at a fixed oxygen partial pressure). Since the depletion region acts as a barrier for electronic charge carrier transport, a material containing p-n junctions would have a much higher effective resistance than that of a pure material.

TABLE 3. Widths of depletion region for various heterojunctions

Heterojunction	L_n (μm)	L_n (μm)	L_p (μm)	L_p (μm)	L_T (μm)	L_T(Cal) (μm)
CuO-SnO_2	0.211	0.199	0.0306	0.038	0.214	0.238
CuO-ZnO	0.289	0.274	0.029	0.040	0.319	0.315
NiO-SnO_2	0.136	0.136	3.208e-4	4.135e-4	0.137	0.137
NiO-ZnO	0.198	0.198	3.82e-4	5.38e-4	0.198	0.198

CuO-SnO_2 heterojunction[6] is used for sensing trace levels of H_2S in ambient air which has higher sensitivity towards reducible gases like H_2S compared to a sensor based on pure SnO_2. Diffusion potential of CuO-SnO_2 heterojunction (0.77eV) is higher than the barrier height due to the chemisorbed oxygen on the pure SnO_2 (0.35eV) and this explains the enhanced sensitivity of CuO-SnO_2 based sensor. From a knowledge of the diffusion potentials arrived at by constructing energy band diagrams, suitable heterojunctions can be incorporated in sensors to enhance their response behaviors.

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