Surface Science 80 (1979) 261–264

WORK FUNCTION AND BAND BENDING ON CLEAN CLEAVED ZINC OXIDE SURFACES

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Absolute values for the work function of the clean cleaved polar and prism faces are given. For freshly cleaved and also for cleaved and annealed oxygen faces band bending and electron affinity are determined. A stable depletion layer is found independent of the annealing temperature, proving the existence of surface states with acceptor character on the clean oxygen face.

1. Introduction

In the hexagonal wurtzite structure three low index planes can be distinguished: The prism surfaces $(10\bar{1}0)$ are found on crystals as grown from the vapour phase or after cleavage parallel to the c axis. The (0001) and $(000\bar{1})$ polar surfaces can be prepared by cleavage normal to the c axis. Accumulation or depletion layers are produced on the n-type crystal by adsorption of atomic hydrogen or of oxygen respectively.

The work function ϕ was measured with a vibrating gold wire (Kelvin method). For absolute values a silicon crystal serving as a reference could be cleaved several times in the same ultrahigh vacuum [1]. Furthermore the surface density ΔN of mobile electrons was determined from surface Hall effect [2].

Table 1

Work function of clean cleaved ZnO surfaces at 300 K

Orientation	Work function (eV)	Electronegativity
$(000\bar{1})$ zinc face	4.25	Zinc 1.5
$(10\bar{1}0)$ prism face	4.64	
$(000\bar{1})$ oxygen face	4.95	Oxygen 3.5
Quadratic deviation	0.05	

2. Work function of the three clean low index surfaces

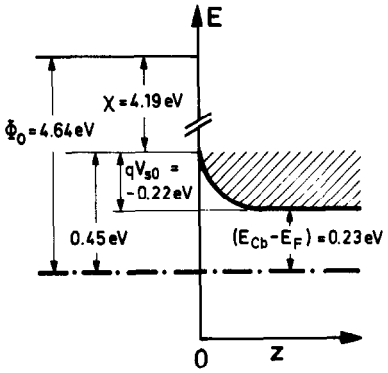
The work function ϕ_0 of freshly cleaved surfaces follows a sequence corresponding to the electronegativities of the atoms [3] prevailing in the uppermost layer (table 1). The work function of the prism face agrees well with a result of Swank: $\phi = 4.68$ eV [4].

3. Band bending and electron affinity of the clean oxygen surface

The position of the Fermi level on clean (111) silicon surfaces was investigated by Allen and Gobeli [1]. They combined work function and photoelectric threshold measurements. However, in the case of zinc oxide the ultraviolet light used in the threshold measurements causes a desorption of lattice oxygen changing the stoichiometry near the surface. The present investigation uses a sequence of work function and surface electron density measurements to determine the position of the Fermi level at the surface.

In the case of accumulation the band bending V_s can be derived by means of a space charge calculation [5] from the surface carrier density ΔN as determined by Hall effect. This method can not be applied in the case of a nearly insulating depletion layer which apparently prevails on clean oxygen surfaces.

However, the band bending of depletion layers can be determined by two successive measurements (figs. 1 and 2): First the work function of the freshly cleaved or



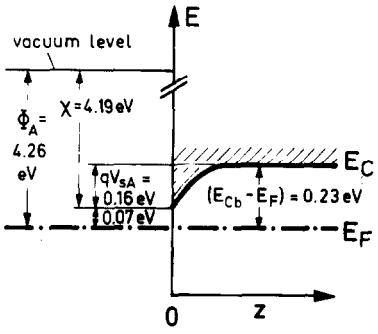


Fig. 1. Energy scheme for the oxygen face of ZnO. After cleavage and also after subsequent annealing in ultrahigh vacuum at temperatures up to 800 K.

Fig. 2. Energy scheme for the oxygen face of ZnO. After cleavage and subsequent treatment with atomic hydrogen at 100 K.

annealed surface is measured at 100 K (see fig. 1):

$$\phi_0 = \chi + (E_{Cb} - E_F) - qV_{s0}.$$

Then a weak accumulation layer is established by atomic hydrogen changing work function and band bending (see fig. 2):

$$\phi_A = \chi + (E_{Cb} - E_F) - qV_{sA}.$$

The index "O" denotes the initial state of the surface, the index "A" the state with an accumulation layer, χ means the electron affinity, $(E_{Cb} - E_F)$ the distance conduction band–Fermi level (bulk Hall effect), and V_s the band bending at the surface. V_{sA} is calculated from the surface carrier density ΔN [5]. Using both equations χ and V_{s0} are accessible.

In the analysis two assumptions are made: The surface donors which are produced by the atomic hydrogen at low temperature are located on the surface. This model is confirmed by space charge calculations and quantitative interpretation of field effect and photoconductivity measurements [5]. Furthermore the

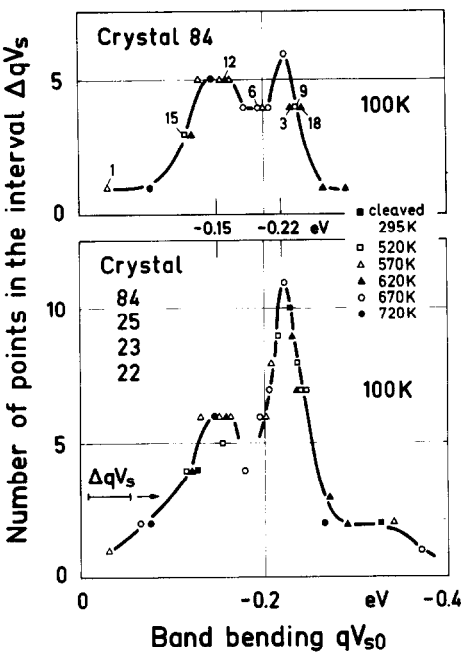


Fig. 3. Band bending qV_{s0} of freshly cleaved and of cleaved and annealed oxygen faces. An energy interval 0.045 eV wide is moved along the band bending scale and the number of points found in this interval is given on the vertical axis. The center of each interval is located at a measured point. The crystals were annealed for 5 min at the temperature indicated by the shape of the point symbols. The sequence in time is marked by numbers at every third point.

electron affinity χ is not affected by hydrogen adsorption in the case of weak accumulation [6].

The derived band bending values are shown in fig. 3. The points are piling up at a depletion of $qV_{s0} = -0.22$ eV and less pronounced at $qV_{s0} = 0.15$ eV. The results of crystal 84 show that both maxima occur already on a single face. From the numbers at the curve it can be deduced, that the shape does not depend on the sequence of pre-treatments. A systematic influence of the annealing temperature can not be recognized. This behaviour might be caused by surface states near or below the Fermi level with $(E_C - E_F)_s = 0.45$ eV as shown in fig. 1 and with $(E_C - E_F)_s = 0.38$ eV. Apparently band bending and the charge in surface states on the freshly cleaved face are not changed by annealing up to 800 K.

The density of these states can not be determined by field effect because the strongly compensated bulk quenches the change of surface conductivity in depletion layers [5]. Only a lower limit of the density can be given from a space charge calculation: $N_{ss} > 10^{11}$ cm^{-2}. Surface states on the oxygen face at 0.57 eV and 0.37 eV below the conduction band are derived by Lüth from surface photoconductivity measurements with infrared light [7].

The present study allows the quantitative determination of band bending for depletion layers in spite of two difficulties: The impossibility of obtaining surface carrier density data for space charge calculations, furthermore the restriction of using ultraviolet light for threshold measurements because of photolysis.

Acknowledgement

The support of the Deutsche Forschungsgemeinschaft via the Sonderforschungsbereich 56 is acknowledged.

References

[1] F. Allen and G. Gobeli, Phys. Rev. 127 (1962) 150.
[2] D. Kohl and G. Heiland, Surface Sci. 63 (1977) 96.
[3] L. Pauling, The Nature of the Chemical Bond (Cornell University Press, 1960).
[4] R.K. Swank, Phys. Rev. 153 (1967) 844.
[5] G. Heiland and D. Kohl, Phys. Status Solidi (a) 49 (1978) 27.
[6] H. Moormann, D. Kohl and G. Heiland, to be published.
[7] H. Lüth, Surface Sci. 37 (1973) 90.