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DOES DIPOLE INDUCE EFFECTS ON HETEROJUNCTIONS ?

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In the last ten years, many efforts have been done to understand the mechanism that regulate the energy level alignment of two semiconductors forming a heterojunction. Several approaches were tested: simple electronegativity considerations applied to low mismatch systems, e.g. Ge/GaAs, lead to good agreement with experimental data^(1,2).

Two fundamental problems have not yet been solved: how important is the microscopic interfacial dipole in determining the band lineup? And in turn, is it possible to change the valence and conduction band discontinuity (ΔE_v , ΔE_c), changing the interfacial dipole?

If the dipole role would be negligible, it should be impossible to change the band alignment. Recent photoemission experiments^(3,4), instead, demonstrate the feasibility of modulating ΔE_v inserting ultrathin layers of different elements at the interface. In particular, cesium and hydrogen, which are sited at opposite sites of the electronegativity scale, show giant effects on ΔE_v in the a-Si/a-SiO₂ heterojunction: hydrogen reduces ΔE_v by 0.4 eV and cesium increases ΔE_v by 0.3 eV.

For the Si/SiO₂ heterostructure, the substrate (30 Å of SiO₂) was obtained evaporating silicon on a silicon cleaved surface held at 250°C and, at the same time, bombarded by oxygen ions, 100 Volts energetics at a 5×10^{-5} Torr partial pressure of oxygen. Amorphous silicon overlayers were electron gun deposited at a rate of 1 Å/min in a base pressure of 3×10^{-10} Torr. This kind of growth probably produces a different interface to that usually achieved oxidizing a silicon wafer, because we didn't observe any intermediate oxidation state of silicon at the interface like those revealed by Hollinger and Himpsel⁽⁵⁾ on the SiO 2p core levels. Moreover, our silica substrate is essentially formed oxidizing amorphous silicon instead of crystalline silicon and, as reported in ref.(6), the amorphous silicon surface, exposed to oxygen, shows higher oxidation sta-

tes than the crystalline one.

Cs intralayer, 0.5 Å thick, was deposited by a "Saes Getter" dispenser on the SiO₂ surface before growing the Si overlayer. Hydrogen was inserted at the interface in three ways:

- exposing the SiO₂ surface to 500 L of hydrogen and then growing the silicon film;
- exposing the Si(5 Å)/SiO₂ interface to the same pressure of hydrogen;
- bombarding the Si(10 Å)/SiO₂ with 100 V energetic hydrogen ions.

We notice that the three methods of hydrogenation always produce the same ΔEv. This strongly support that the ΔEv variation is due to the interface chemistry. We interpret such variations of ΔEv as due to variations of the microscopic dipole.

We calculate the interfacial dipole voltage Vd, considering two plane distributions of charge at the interface. In our case, the two semiconductors are amorphous and their surface densities are calculated from the bulk densities. The difference between the two surface densities gives the density of silicon atoms not in contact with silica molecules. These sites are available for bonding hydrogen or cesium intralayer atoms, determining an extra field responsible for the valence band discontinuity variations.

To evaluate the surface charge distribution in the planes parallel to the interface, we applied the Sanderson criterion that assumes the same, averaged, electronegativity of atoms and molecules forming compounds^(7,8). The calculation gives a transfer of 0.18 electrons per atom from silicon to silica, and 0.10 and -0.55 electrons from silicon to hydrogen and cesium respectively.

We schematized the heterojunction as two semiinfinite chains of Si atoms and SiO₂ molecules whose radii are deduced from the covalent radius and the average bulk density respectively. The uncovered area of silicon is represented by a chain truncated to the last silicon or adsorbed atom.

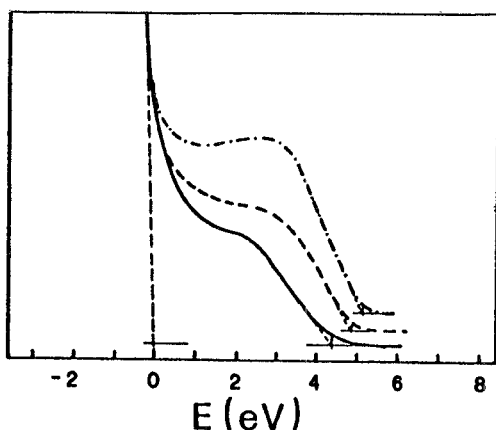


Fig. 1 - Energy Distribution Curves (EDC) of Si/SiO₂ (---), Si/Cs/SiO₂ (-·-·-), and Si/H/SiO₂ (—), taken at 41 eV of photon energy and aligned to the SiO photoemission leading edge. The Valence Band Discontinuities (ΔEv) are measured by the energy difference of the leading edges of Si and SiO₂ (broken lines). Only the region near the top of the valence band is shown.

An exponential decay of charge, far from the interface, is assumed imposing that the sum of all the components of the chain, must be equal to the charge exchanged between a single couple Si-SiO₂ (0.18 e), and the first terms of the two series are calculated applying the Sanderson formula (9).

Every element of the chains have a charged plane associated generating an electrostatic field $E=\sigma/2\epsilon$. The sum of all the fields, gives the dipole voltage variations reported in Table I. In the same Table, we report the experimental ΔE_v variations. We found a good agreement between ΔE_v and ΔV_d in both sign and magnitude, indicating a good reliability of the model.

TABLE I

Heterojunction	Intralayer	ΔE_v	ΔV_d
Si/SiO ₂	none	4.90	----
Si/SiO ₂	H	4.40	+0.3
Si/SiO ₂	Cs	5.15	-0.2

This simple model, doesn't pretend to be the solution of the bands discontinuity problem but it can be a "low order approximation" of more sophisticated approaches.

References:

- (1) W.R.Frenley and H.Kroemer, Phys. Rev. B16, 2642 (1977).
- (2) W.A.Harrison and E.A.Kraut, Phys. Rev. B18, 4402 (1978).
- (3) F.Capasso, A.Y.Cho, K.Mohamed and p.W.Foy, Appl. Phys. Letters 46, 664 (1985).
- (4) D.W.Niles, G.Margaritondo, P.Perfetti, C.Quaresima and M.Capozzi, Appl. Phys. Letters 47, 1092 (1985).
- (5) G.Hollinger and F.J.Himpfel, Appl. Phys. Letters 44, 93 (1983).
- (6) R.A.Riedel, M.Turowski, G.Margaritondo, P.Perfetti and C.Quaresima, J. Appl. Phys. 55, 3195 (1984).
- (7) R.T.Sanderson, Inorganic Chemistry (Reinhold, 1967).
- (8) R.T.Sanderson, Chemical Bonds and Bond Energy (Academic Press, 1971).
- (9) J.C.Carver, R.C.Gray and D.M.Hercules, J. Ann. Chem. Soc. 96, 6851 (1974).