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Interplay of bonding and electronic properties at diamond interfaces

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Outline :

- 1. What quantities govern the potential barrier height at metal/oxygenated (100) oriented diamond interfaces ?**
- 2. Interface states and bonding at dielectric /oxygenated (100) oriented diamond interfaces**
- 3. Conclusions**

1. 1. Assessment of ideal barrier heights at Schottky interfaces

The non-ideal current density under junction voltage V_j of the Schottky diode with a barrier height Φ_B^0 at $V_j = 0$ and a non-ideality factor n is:

$$J_z = \alpha A^{**} T^2 \exp\left(-\frac{e_0 \Phi_B^0}{k_B T}\right) \left[\exp\left(\frac{e_0 V_j}{n k_B T}\right) - 1 \right] \quad (1)$$

Alternatively, it can be expressed as an ideal thermoionic current density with a voltage and temperature dependent barrier height $\Phi_B(T, V_j)$, due to barrier inhomogeneities, image force lowering, etc:

$$J_z = \alpha A^{**} T^2 \exp\left(-\frac{e_0 \Phi_B(T, V_j)}{k_B T}\right) \left[\exp\left(\frac{e_0 V_j}{k_B T}\right) - 1 \right] \quad (2)$$

Whenever the reverse current can be neglected, one gets from the two previous equations:

$$\frac{k_B T}{e_0} \frac{d(\ln J_z)}{dV_j} = \frac{1}{n(T, V_j)} = 1 - \frac{d\Phi_B(T, V_j)}{dV_j} = 1 + \frac{d\Phi_B(T, U)}{dU} \quad (3)$$

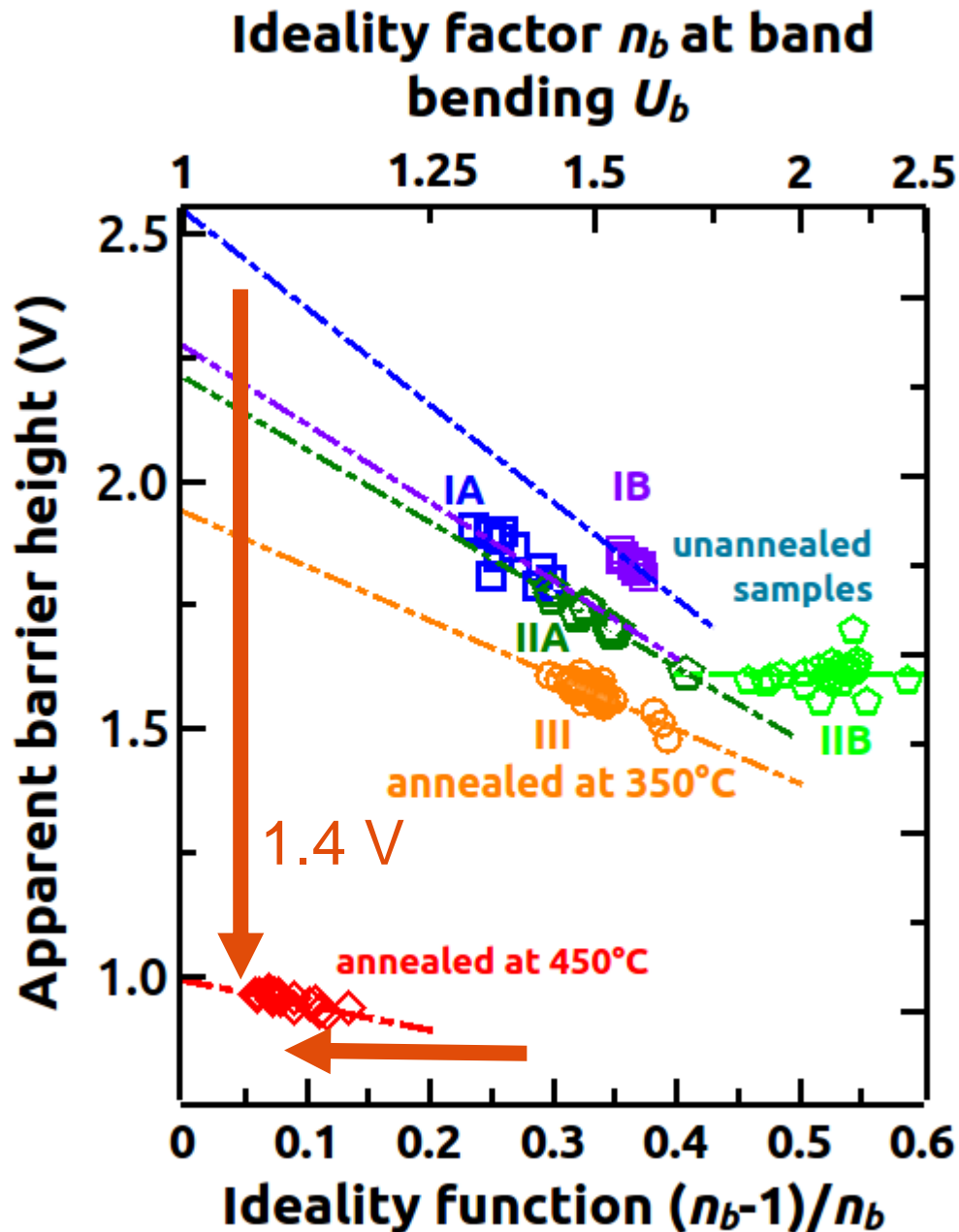
where U is the band bending inside the depletion zone.

The ideality factor is therefore voltage dependent in general.

But if there is a voltage range near V_b and band bending U_b where this dependence is negligible, extending over U_b/K , integration of the second and fourth expressions gives:

$$\Phi_B^{app}(T, U_b) = \Phi_B^{ideal} - \frac{U_b}{K} \frac{n(T, U_b) - 1}{n(T, U_b)} \quad (4)$$

1.2. Ideal barriers in Zr / initially oxidized (100) diamond surfaces

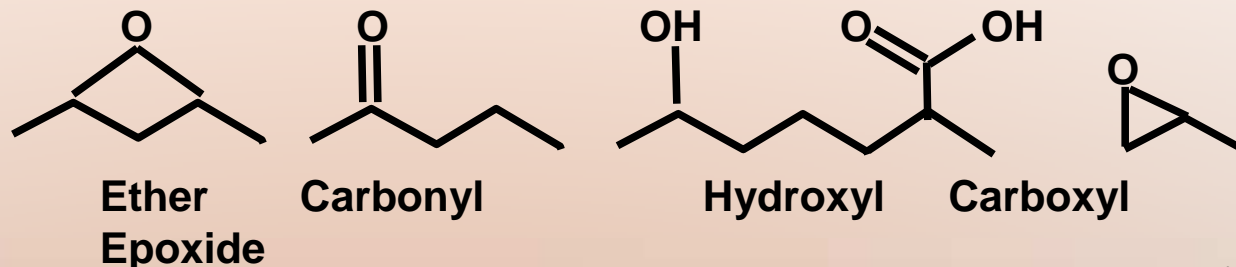


I, II & III are distinct samples

- two different ideal barriers in the unique sample I ;
- almost the same ideal barrier in two different samples (groups of data IA & IIA)
- annealing at 450°C reduces the barrier by 1.4 V in average, and strongly decreases the ideality factor

1.4. Comparison with other known properties of the oxygenated surface and metal interfaces

♦ dispersion of the oxygen terminations \Rightarrow



♦ non homogeneity of (i) the oxide interlayer and possibly (ii) bonding with metal before annealing \Rightarrow

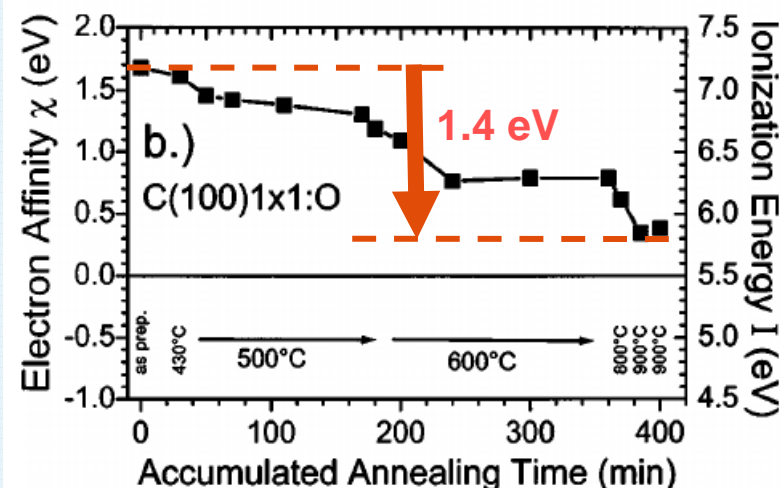
See TEM studies by J. Pinero, D. Araujo and co-workers

♦ same change in Electron Affinity by $\Delta\chi = 1.4 \text{ eV}$ after annealing \Rightarrow

♦ also evidenced in four other metals (Mo, Au, Pt, Al) on the initially oxygenated (100) surface

(Studies by AIST, NIMS & French groups since 2009)

♦ theoretical calculations give rather $\Delta\chi \geq 3 \text{ eV}$ unless H is present \Rightarrow



J. Ristein et al., J. Electrochem. Soc. 151(2004)E315 and Saby & Muret SST 19(2004)1

S.J. Sque et al PRB73(2006)085313 ; J. Robertson et al DRM7(1998)620

1.5. Barrier height models

● Metal- or interface-induced gap states (assumed independent of the metal)

$$e_0 \Phi_{Bp}^{hom} = \Phi_0 + S_\phi [(I_{SC} - \Phi_0) - \phi_m] \text{ where}$$

$$S_\phi = \frac{A_\phi}{1 + (e_0^2 / \epsilon_i \epsilon_0) D_{is} d_{di}} > 0$$

Inappropriate

● Bond-induced interface dipole

With $I_{SC}(S) = E_G + \chi + \Delta\chi(S)$,
 Δq the charge transfer on the metal side,
 d_{bd} the bond length and N_{bd} the number of bonds:

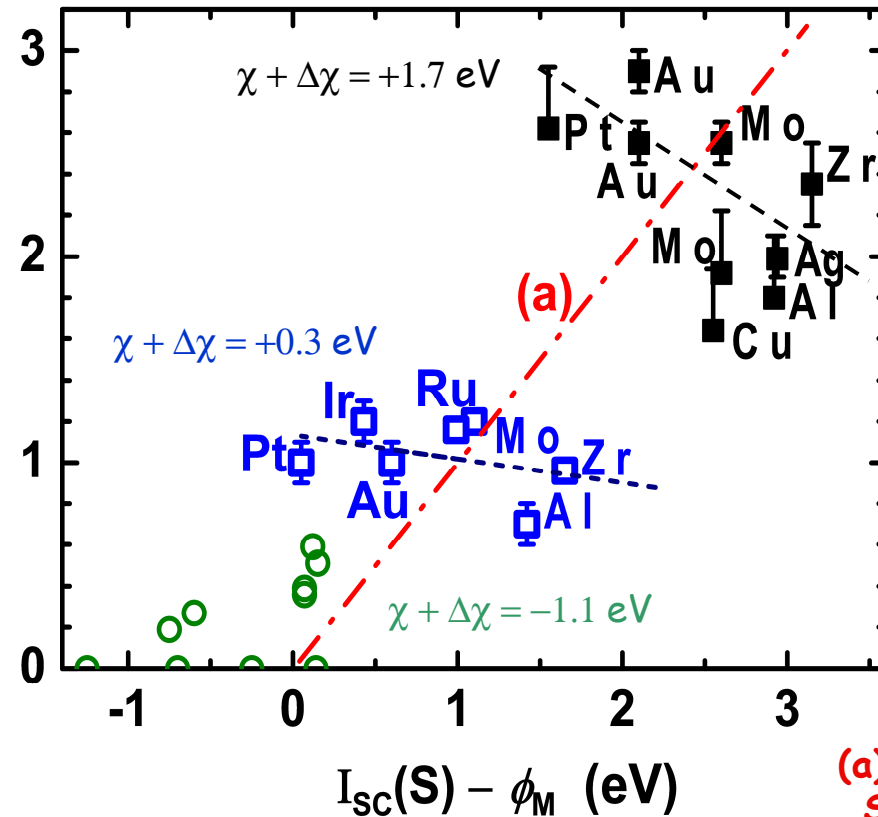
$$e_0 \Phi_{Bp}^{hom} = (I_{SC}(S) - \phi_M) - e_0 \Delta q d_{bd} N_{bd} / (\epsilon_i \epsilon_0)$$

If one defines the abscissa $W_{SM} = (I_{SC}(S) - \phi_M)$, the slope is:

$$\frac{d(e_0 \Phi_{Bp}^{hom})}{dW_{SM}} = 1 + \frac{d(e_0 \Delta q d_{bd} N_{bd} / (\epsilon_i \epsilon_0))}{d\phi_M}$$

The more electronegative metal (& ϕ_m), the less Δq , \Rightarrow second term < 0

Ideal barrier heights $e_0 \Phi_{Bp}^{hom}$ (eV)



Experimental data for non-annealed interfaces ; slope ≈ -0.4

same for annealed interfaces ; slope ≈ -0.13

hydrogenated interfaces

(a) = Mott-Schottky relationship

More in arXiv: 1501.04790 , submitted to JAP

The bond-induced dipole model is able to explain both positive and negative slopes. Strong change of the bonds C-O and C-metal at interface occurs after annealing.

2.1. Electrical properties of MIS structures (oxide states)

$$V_G = V_{FB} - \frac{1}{C_{ox}} (Q_{SC} + Q_{is}(\phi_{s0})) + \phi_s \quad (1a)$$

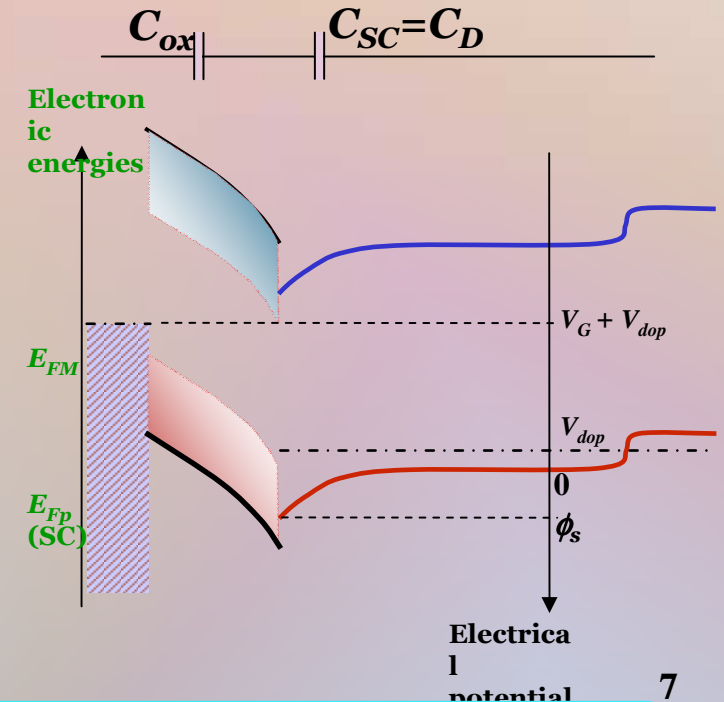
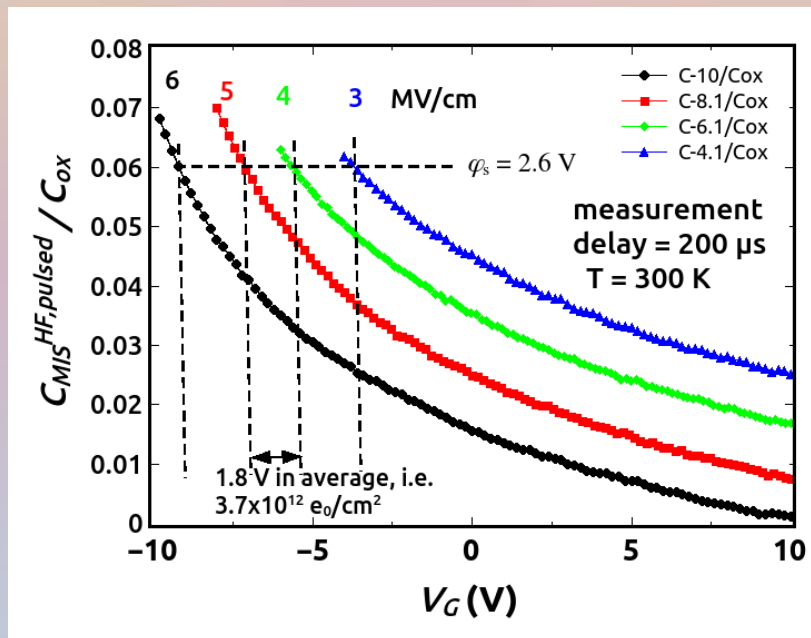
where the theoretical flat band voltage V_{FB} is defined at $\phi_{s0} = 0$:

$$V_{FB} = \Phi_{MS} - (Q_{is}(0) + \overline{Q_{ox}}) / C_{ox} \quad (1b)$$

In the depletion regime after delay d and with $q = -|e_0|$ for a p-type semiconductor:

$$(C_{MIS}^{HF})^{-2} - (C_{ox})^{-2} = \frac{2}{q\epsilon_{SC}N_{di}} [V_{FB} - Q_{is}^d(\phi_s)/C_{ox} - V_G] \quad (2)$$

The pulse HF capacitance method performs each measurement with a constant initial condition, as close as possible to flat band, after a constant delay d :



Improvement of the insulator crystallinity and quality needed

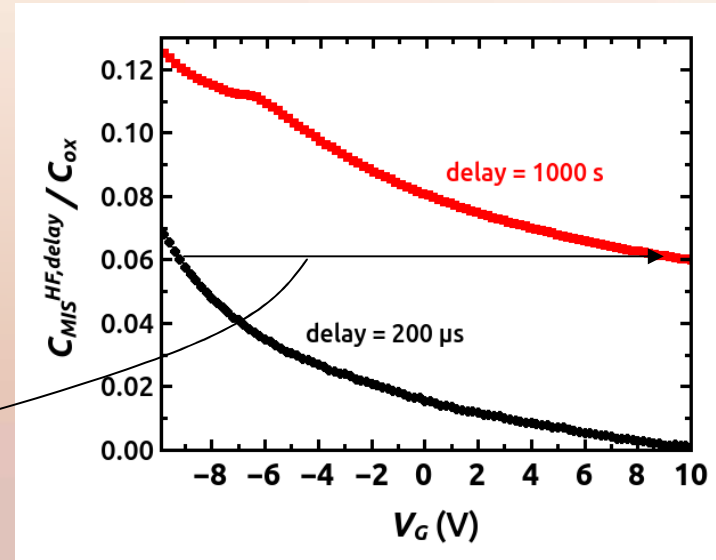
2.2. Electrical properties of MIS structures (interface states)

The pulse HF capacitance method applied with different measurement delays at constant capacitance:

$$V_G^{d0} = V_{FB} - \frac{1}{C_{ox}} \left(Q_{SC} + Q_{is}^{d0} \right) + \phi_s$$

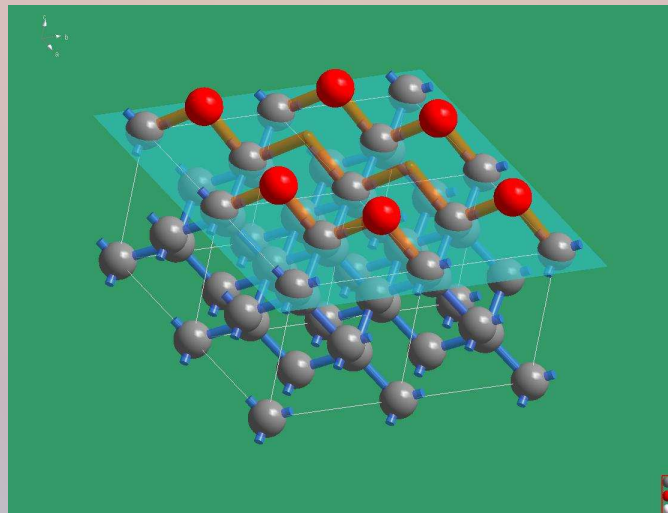
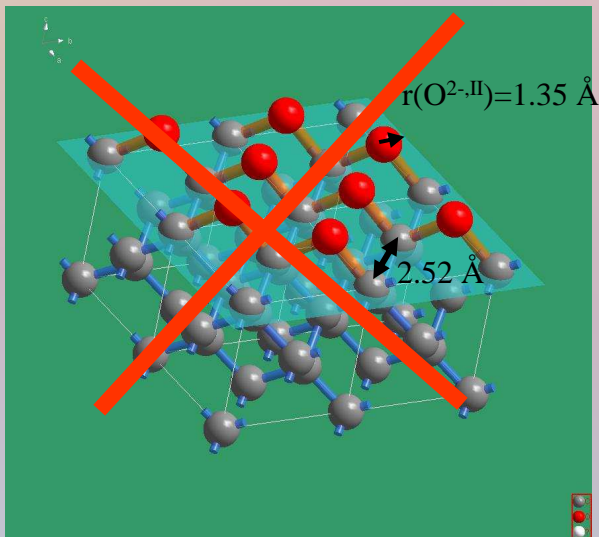
$$V_G^{d1} = V_{FB} - \frac{1}{C_{ox}} \left(Q_{SC} + Q_{is}^{d1} \right) + \phi_s$$

$$C_{ox} \times 18 \text{ V} = 3.7 \times 10^{13} \text{ e}_0/\text{cm}^2$$



$T = 300 \text{ K}$

The probable origin of interface states:



Unsaturated bonds, mainly due to reconstructed or dangling carbon orbitals likely remain and are responsible for interface states within the bandgap.

Current directions of research:

- Improvement of the crystalline quality of the insulator and increase of its bandgap (maybe other candidates such as SiO_2 or CaF_2 would show better properties);
- pre- and post-treatments of the interface (thermal annealing or plasma treatment under various gas containing O, F, H species) dedicated to the decrease of interface states.

Conclusions

Methods able to investigate interface properties have been implemented.

Bonding at interface controls the most important quantities like potential barriers and interface states. Progress toward a fully operative MOS transistor are going on.

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