# CVD Diamond Surface Characterization and Contact Interface Properties

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# Outline

- 1) Introduction: The Ideal Schottky Contact Theory
- 2) Atomic Arrangement of Diamond Surface ((111) and (100))
- 3) Electron Affinities of Diamond
- 4) Surface Geometrical Properties
- 5) Surface Defects of clean, O and H terminated diamond
- 6) Fermi-level determination by Kelvin Force Experiments
- 7) Surface electronic properties
- 8) The electronic Density of State Distribution at the surface
- 9) Contact Properties to Diamond







### 1. Introduction: Schottky Contact Theory



Schottky Barrier Hight:

 $q\Phi_{Bn} = q(\Phi_m - \chi)$ 

Metal Workfunction  $\Phi_{m}$ Two Parameter: Electron Affinity of Semiconductor  $\chi$ 







Fig. 4 Metal work function for a clean metal surface in a vacuum versus atomic number. Note the periodic nature of the increase and decrease of the work functions within each group. (After Michaelson, Ref. 9.)



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Example Au, which is used as a calibration standard in Photo-Yield experiments:

Au Textbook data: 5.2 eV

Experimentally detected: 4.3

What to take in reality?







# 2. Geometry of Diamond Surface: (111) Diamond



Fig. 19. Schematic representation of building blocks forming diamond (001) surfaces. (a) Clean  $(1 \ 1 \ 1) - 2 \times 1$  structure where dangling bonds are involved to form  $\pi$ -bonded dimers. (b)  $(1 \ 1 \ 1) - 1 \times 1$ :H structure composed of monohydride dimers where each dangling bond per carbon atom is terminated by hydrogen. (c)  $(1 \ 1 \ 1)$  Trihydride structure where each dangling bond per carbon atom is terminated by trihydride carbon.



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# (001) Diamond Surface



Fig. 12. Schematic representation of building blocks forming diamond (001) surfaces. (a) Clean (001)-2 × 1 structure where dangling bonds are involved to form  $\pi$ -bonded dimers. (b) (001)-2 × 1:H structure composed of monohydride dimers where each dangling bond per carbon atom is terminated by hydrogen. (c) (001)-2 × 1:2H structure where two dangling bonds per carbon atom are terminated by hydrogen.

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Natural single crystal (100) diamond after annealing at 1.100 °C

STM Result



Figure 2 Clean diamond C(100)–(2×1) surface. **a**, The STM topography (10 mm× 10 nm) of the clean diamond surface recorded in the near-field emission regime ( $U_{\rm bas} = 5.9$ V, l = 1.1 nA). **b**, Height variation of the STM tip along the line A. **c**, Topview of a monoatomic step on the two-domain (2×1) reconstructed surface. The coloured circles represent the carbon atoms belonging to the top four surface layers; the biggest circles represent the carbon–carbon dimers. The domains labelled as I and II represent the upper and lower terrace, respectively. The dimer rows are highlighted by shading, whereas the troughs between them are unfilled. The dashed line shows schematically the boundary between the domains.



H-free surface, clean diamond

(2x1) reconstruction with  $\pi$ -bondet dimers



K. Bobrov, G. Dujardin, et al., Nature 413, 616 (2001)

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# STM topography of hydrogenated C(100)-(2x1):H

CH-dimer rows without (a) and with one defect (b)



Fig. 2. Desorption of individual hydrogen atoms from the hydrogenated diamond C(100)-(2 × 1):H surface. The corresponding STM topographies ( $2.1 \times 2.6 \text{ nm}$ ), before (a) and after (b) the desorption procedure, were recorded at  $U_{\text{bias}} = -1.5 \text{ V}$ ,  $I_t = 1.0 \text{ nA}$ . The bright feature visible in (b) represents the dangling bonds after desorption of individual hydrogen atoms.

#### Hydrogen desorption by pulsed voltage to the STM Tip (b)

K. Bobrov, G. Dujardin, et al. Surface Science 528, p. 138 (2003)





# STM topography oh hydrogenated natural C(100)-(2x1):H

H-termination has been done ex-situ at 800 °C, for 1h

a): Atomically flat surface with mono-atomic steps





K. Bobrov, G. Dujardin, et al. Surface Science 528, p. 138 (2003)



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# 3. Electron Affinities of Diamond





Data from:

#### Electron Affinities of Diamond: Mixed Surface Properties

Vacuum level variations from -1.1 to +1.7 eV ( $\Delta E = 2.8 \text{ eV}$ )

For partially H-terminated diamond, where is the vacuum level?





C(100)-(1x1):O



FIG. 6. Electron affinity  $\chi$  versus oxygen coverage; the solid line is a fit to the data with a dipole moment  $p_z = -0.10 \ e$  Å and a polarizability  $\alpha = 2.0 \times 10^{-30} \text{Asm}^2/\text{V}$  (see text).

F. Maier et al. Phys. Rev. B 64, 165411 (2001)



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### **Electron Affinities of Diamond Surface**

TABLE I. Summary of electron affinities of clean, hydrogen and oxygen covered diamond surfaces. (sc: natural single crystal type IIb; homo: homoepitaxial boron doped CVD-film; HF-H *in situ* hydrogenation via hot filament; P-H/P-O: *ex situ* plasma hydrogenation/oxidation; UHV-A: Annealing in UHV).

Diamond	Sample Preparation	$\chi$ in eV	Reference
(111)-(2×1)	sc UHV-A	≈0.5	11
	sc UHV-A	0.5	14
	sc UHV-A(1000 K)	0.38	16
	sc UHV-A	1.5	15
(111)-(1×1):H	sc HF-H	≤-0.7	11
	sc chem. oxidized, P-H	<0	14
	sc P-H	≤-0.9	15
	sc P-H	-1.27	16
(111) graphitized	sc UHV-A(1400 K)	0.80	17
(111)-(2×1)	theory	0.35	18
(111)-(1×1):H	theory	-2.03	18
(100)-(2×1)	sc UHV-A	0.75	14
	sc UHV-A	1.3	15
	sc UHV-A	0.5	this work
(100)-(2×1):H	sc P-H	$\approx -0.8$	12
	sc HF-H	$\approx -0.4$	13
	sc P-H	≤-1.0	15
	homo P-H	0.19	7
	sc P-H	-1.3	this work
(100)-(1×1):O	sc chem. oxidized	$\approx 1.0 - 1.5$	14
	homo P-O	≈0.64	7
	sc chem. oxidized	1.7	this work
$(100)-(2\times1)$	theory	0.51	18
(100)-(2×1):H	theory	-2.05	18
(100)-(1×1): O <sub>other</sub>	theory	2.61	18
(100)-(1×1): O <sub>ketone</sub>	theory	3.64	18

F. Maier et al., Phys. Rev. B 64, 165411 (2001)





# 4. Surface Geometrical Properties





# Diamond Surface: Poly CVD Diamond



## Diamond after polishing

Polishing Roughness: 8 - 15 nm

Electronic Properties are bad, due to defects, generated by polishing !

No electronic grade interface !











# Homo-epitaxial Growth of CVD Diamond (AIST)



Fig. 1. Map of the surface morphology as a function of both the misorientation angle and the  $CH_4/H_2$  ratio.<sup>(1)</sup> The dotted lines in the figure serve as a guide to the eye and are used to divide the area into four regions I–IV. A detailed explanation is given in the text.

H. Watanabe et al., New Diamond and Frontier Carbon Technology, 12, 369 (2002)



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### Homo-epitaxial Growth of CVD Diamond (AIST)







ig. 2. Typical surface morphologies of the homoepitaxial diamond film in region III in Fig. 1. (a) a top-view AFM image (200 nm  $\times$  200 nm  $\times$  0.5 m) the surface morphology for the misorientation angle of  $0.4^{\circ}$  at 0.025% CH<sub>4</sub> /H<sub>2</sub> ratio for 42 h deposition, and (b) a top-view AFM image (1  $\mu \times 1 \mu \times 0.5$  nm) for the misorientation angle of 0.2° at 0.025% CH<sub>4</sub>/H<sub>2</sub> ratio for 6 h deposition.

> Atomically flat surface with step-etch growth. Terraces run parallel to the (110) direction

> > National Institute of

H.Okushi, Diam. Rel. Mat. 10, 281 (2001)





# Bulk Properties of Homo-epitaxial CVD Diamond



Free exciton emission lines at: 235 nm (5.27 eV) and 242 nm (5.12 eV)

High bulk electronic property indication!



Fig. 3. Near-band-edge CL spectra at room temperature, where (a): the spectrum for the diamond film and (b): the Ib diamond substrate [8].





# 5. Surface Defects of clean, O and H terminated diamond





# Surface Fermi Level on (111)-(2x1) reconstructed Diamond

Photoelectron yield and core level photoemission spectroscopy



Diamond (111) 2x1

J.B. Cui et al. Phys. Rev. Lett. 81, 429 (1998)





# Oxidation





### Wet-Chemical Oxidation



Oxygen Coverage (111) by XPS: ca 50 %

Boiling in:  $HNO_3:H_2SO_4 = 1:3$ at 230 °C for 1 h





#### Properties:

- insulating surface
- hydrophilic
- removement of graphitic layers (at grain boundaries)
- Fermi-level pinning at the surface due to defects?





#### Surface defect density of O-terminated diamond surface

#### Before SiO<sub>2</sub>-deposition

1) plasma-ashed in 2%  $O_2$  in He 2) cleaned at 200 °C in solution of  $(NH_4)_2S_2O_8$  and  $H_2SO_4$ 

SiO<sub>2</sub> Deposition:

atmospheric pressure CVD using SiH<sub>4</sub>, Ar, N<sub>2</sub> and O<sub>2</sub> T= 625 °C on (100) diamond

Surprisingly good interface !

M.W. Geis et al. IEEE Trans. Electron Dev. 38, 619 (1991)



Fig. 8. Energy diagram of metal-SiO<sub>2</sub>-diamond structure for (100)-oriented substrate.  $E_C$  is the minimum energy of electrons in the conduction band,  $E_v$  is the maximum energy of electrons in the valence band, and  $E_F$ is the Fermi energy level. A lower estimate of the positive interface trap level density is plotted versus energy (the energy axis coincides with the SiO<sub>2</sub>-diamond interface).

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Fig. 19 Interface-trap density in thermally oxidized silicon. (After White and Cricchi, Ref. 27.)

Sze, in "Physics of Semiconductor Devices"



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# Hydrogen Termination





# H-termination



# IR-Properties (characterized in air)



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## SEM image of Bar-Contact structures



partially wiped in ethanol





#### Cleaning by contact mode AFM



Surface is covered with a thin

- (1 -10) nm thick adhesive layer.
- Removal Force: 1mN/100 nm<sup>2</sup>
- Non-conductive layer !

B. Rezek, C.E. Nebel, M. Stutzmann Diam. and Rel. Mat. 13, 740-745 (2004)







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# Wetting Angle Experiments on H-terminated diamond





# H-term. CVD diamond

After hydrogen plasma treatment:





**80**°

SEM After mechanical cleaning in Ethanol: wetting angle (1ul droplet)





**95**°



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# AFM – carbon deposit in air and liquids (e788)












## pH Sensitivity of Intrinsic Diamond: Virtual Gate-Insulator







#### **Electrostatic Attraction of Ionized Nano-Particles**

Accumulation of charged particles on the surface, in the water adsorbate?

Due to electrostatic force, only small particles will be attached

•CH Dipole

•CO Dipole









#### 6. Fermi-level determination by Kelvin Force Experiments

#### **Current detection**

$$I = \frac{dQ}{dt} = \frac{1}{dt} \left\{ C \left[ -(\phi_1 - \phi_2) + U_{comp} \right] \right\}$$
  
For I = 0

$$\phi_1 - \phi_2 = U_{comp}$$

Kelvin Force Microscopy:

$$F_{z} = \frac{1}{2} \frac{dC}{dz} U^{2}$$

$$F_{\omega} = \frac{dC}{dz} \left[ -(\phi_{1} - \phi_{2}) + U_{comp} \right] = 0$$

$$\phi_{1} - \phi_{2} = U_{comp}$$



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### Kelvin-Force Microscopy:





### Kelvin Force Microscopy on Hydrogen Terminated Diamond



## Surface Energy Diagram of H-Terminated Diamond



#### KFM on AI / Au / H-Terminated Diamond



Work-function difference: AI / Au or AI / H-Term-Diamond: 590 meV



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## AI on H-Terminated Diamond



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## 2D Aluminum-Schottky Junction to H-terminated diamond









## 7. Surface electronic properties





## Secondary Photoelectron Emission Spectra on intrinsic (100), n- (111) and p- (111) type diamond





Negative electron affinity:  $\chi = E_g - E_{th} = 5.47 \text{ eV} - 4.4 \text{ eV} = -1.07 \text{ eV}$ 



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Spectrally Resolved Photoconductivity (SPC)

**Contact Arrangement** 

 $100 \ \mu m \ x \ 500 \ \mu m$ 







#### Contact Size for SPC:











## Typical SPC on H-terminated Diamond







#### Other sample, H-terminated



File: Bohus sample Folder: Ergebnisse/Surface functionalization/H-termination/Bohus Sample







File: Bohus sample Folder: Ergebnisse/Surface functionalization/H-termination/Bohus Sample



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#### Comparision: H-term to Oxidized



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## Comparison with TPYS





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#### Hole Generation



# 8) The electronic Density of State Distribution at the surface





#### Electronic properties of H-term. diamond surface



#### One dimensional numerical solution of Schrödinger and Poisson Equations:

Effective confinement potential:



Schrödinger Eq. (BenDaniel-Duke form):

$$-\frac{\hbar^2}{2}\frac{d}{dx}\frac{1}{m(x)}\frac{d\phi_i(x)}{dx}+V(x)\phi_i(x)=E_i\phi_i(x)$$

Poisson's Eq.

 $\frac{d}{dx}\varepsilon_{o}\varepsilon_{r}(x)\frac{d\phi(x)}{dx}=e\sum_{i}N_{i}\phi_{i}(x)-\rho_{I}(x)$ 

Number of holes per unit area in sub-band i:

$$N_{i} = \frac{mkT}{\pi\hbar^{2}} ln \left[ 1 + exp\left(\frac{E_{F} - E_{i}}{kT}\right) \right]$$

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#### Valence Band Structure of Diamond

#### Parameters used:



Result for 5x10<sup>12</sup> cm<sup>-2</sup> sheet hole density:



Diam. and Rel. Mat. Vol 13/11-12, 2031-2036 (2004).



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#### **Disorder Induced Localization of States:**



- 1) Hydrogen Termination not Perfect
- 2) Ionic Effects of Adsorbate Layer
- 3) Surface Roughness





#### H-term. Diamond Surface

#### Disorder-Effects



#### Activation Energy in the Miniband







## 9. Contact Properties to Diamond





#### Ideal Schottky Contact







#### Capacitance-Voltage Measurements on Metal-SiO<sub>2</sub>-Diamond (100)



Fig. 8. Energy diagram of metal-SiO<sub>2</sub>-diamond structure for (100)-oriented substrate.  $E_C$  is the minimum energy of electrons in the conduction band,  $E_{\nu}$  is the maximum energy of electrons in the valence band, and  $E_F$ is the Fermi energy level. A lower estimate of the positive interface trap level density is plotted versus energy (the energy axis coincides with the SiO<sub>2</sub>-diamond interface).

M.W. Geis et al, IEEE Transactions on Electron Devices 38, 619 (1991





#### **Real Schottky Contact**







#### Schottky Barrier Hight

(W. Moench, in Semiconductor Surface and Interfaces, Springer1995, p. 368



CNL = Charge Neutrality Level







## Thermal annealing of Ti on Boron-Doped Diamond

Boron doped CVD diamond: (3-6)x10<sup>17</sup> cm<sup>-3</sup> B-concentration

Ti/Pt/Au contacts

annealed in Ar

for 30 minutes







#### Specific Contact Resistance of: Ti, Mo, Cr, Pd, Co

#### Annealing

Ti	(400 °C 5 min)
Мо	(600 °C, 60 min)
Cr	(600 °C, 10 min)
Pd	(600 °C, 10 min)
Со	(600 °C, 10 min)

in vacuum

optimized annealing conditions.



FIG. 5. Specific contact resistances of the Ti, Mo, Cr, Pd, and Co contact before and after annealing vs  $N_A^{-1/2}$  at room temperature.

M. Yokoba et al., JAP 81, 6815 (1997)







# Formation of thermally stable graphite layer during annealing

Formation of
1) Cr<sub>3</sub>C<sub>2</sub>
2) Graphite

At the interface



FIG. 4. A high-resolution lattice image of the diamond/Cr interface after annealing at 600 °C for 10 min.

M. Yokoba et al., JAP 81, 6815 (1997)






## God invented "BULK PROPERTIES"

The Devil: THE SURFACE !





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