Diamond for high frequency devices, DNA sensors and superconductor

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1. **Doping technologies realizing highly conductive diamond for new device application**
2. **High frequency devices based on interface properties**
3. **DNA sensors for 1 base mismatch detection using diamond surface by fluorescence and transistors**

Toward lighter element

III IV V

Two findings are an indication of coming a carbon century

B C N

1990 Carbon Nanotubes found in electron microscopy

1983 Diamond formed from gas phase

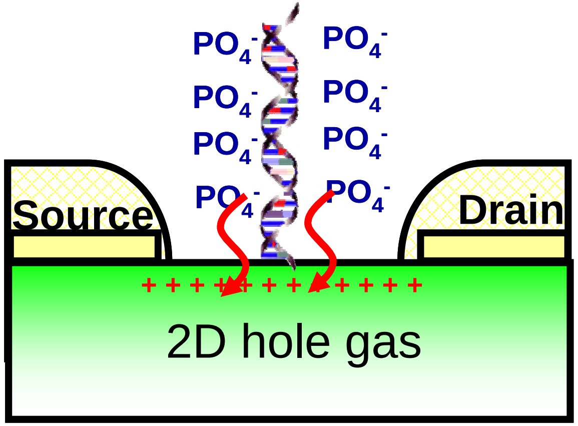
Al Si P

1960 Development of Transistors, ICs

Ga Ge As

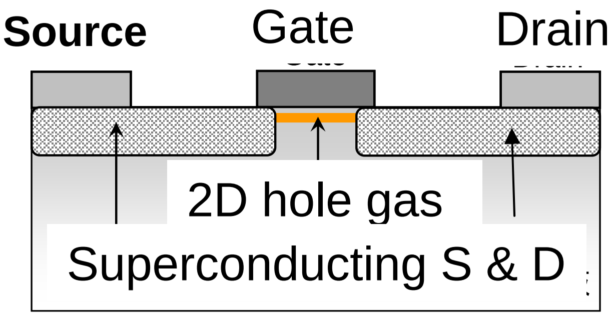
1947 Invention of Transistors

Carbon based nano and bioelectronics in Kawarada's group



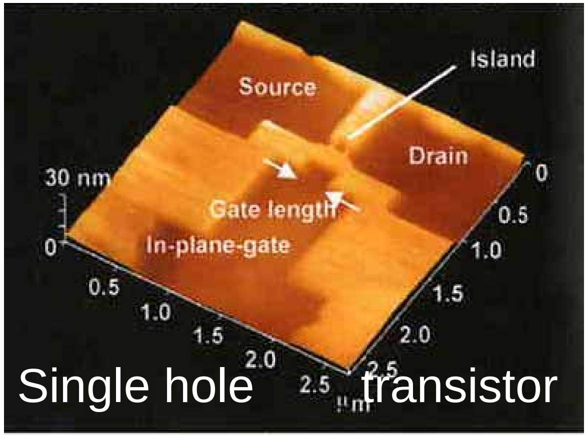
1.Microwave devices
and their characteristics
-Diamond MOSFET
f_T 45 GHz, f_{max} 100GHz

IEEE Elect. Dev. Lett, **22**, 390 (2001)
23, 121(2002), **25**, 480(2004)
Appl. Phys. Lett. **88**, 112117 (2006)



3. Biosensor & bioelectronics
-Surface chemical modification
-Diamond solution gate FETs
for Biosensing DNA detection

Phys.Rev.E. **74**, 041919 (2006)
Langmuir, **22**, 11245 (2006)
Appl. Phys. Lett. **90**, 063901 (2007) .

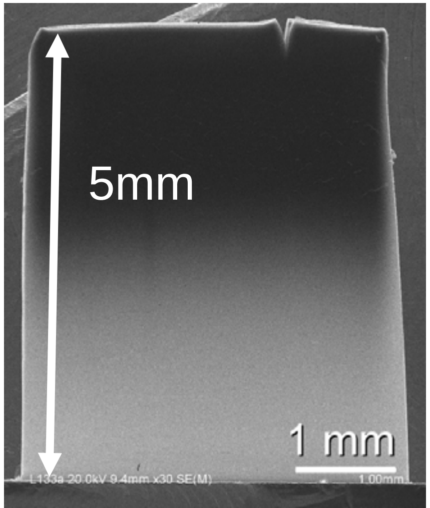


Single hole transistor

Appl. Phys. Lett., **81**, 2854 (2002).

2.Superconductivity
and transistor application
Highly B-doped >$10^{21}cm^{-3}$
Diamond Tc ~10K
Cryoelectronics

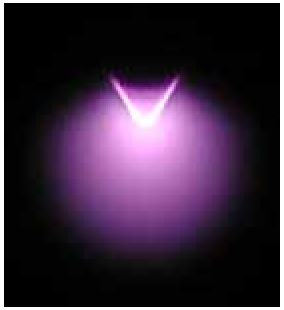
Y.Takano, H. Kawarada, et al.
Appl. Phys. Lett. **85**, 2851(2004)
T. Yokoya, H. Kawarada, et al.
Nature, **438**, 647-650 (2005)



4. Carbon nanotubes
Densely packed & vertically oriented
single or double wall carbon nanotube
for interconnection and super capacitor

J. Phys. Chem. B, **109**, 19556 (2005)
Carbon, **44**, 2009 (2006)
J. Phys. Chem. B, **111**, 1907 (2007)

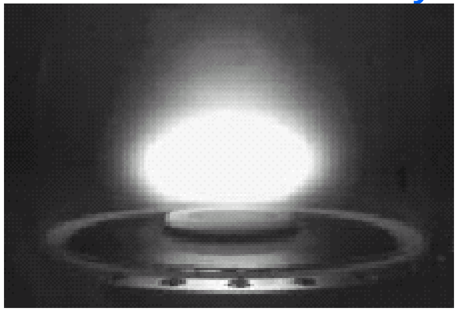
State of art
plasma
deposition



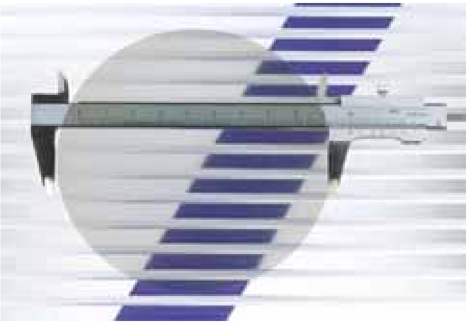
Poly crystalline diamond substrate

Courtesy from Fraunhofer Institute, Freiburg

Ellipsoidal Microwave Plasma Reactor

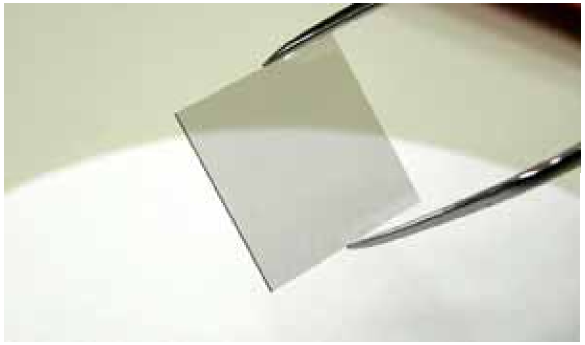


Plasma cloud
in the vicinity of substrate



CVD diamond wafer
with diameter of 10 cm

Various kind of
CVD diamond



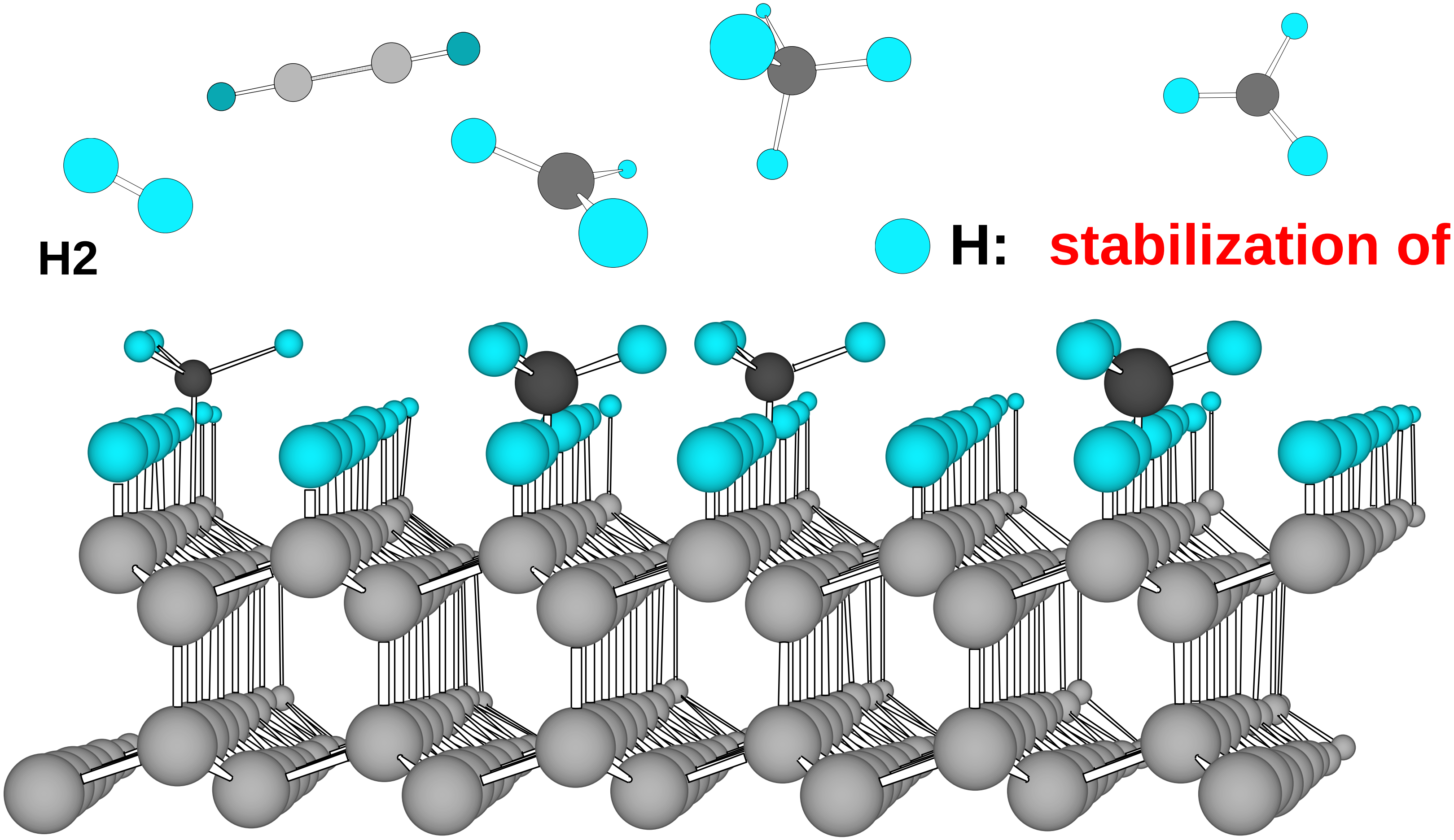
Diamond chip (5 by 5 mm)

Plasma Decomposition of CH4 and H2

CH3 and H radicals

Diamond or Carbon Nanotube

Diamond surface during growth



CH4:methane

CH3 : methyl radicals

C2H2

H2

● H: stabilization of sp^3

Outline for Subject 1 and 2

- **Semi- and Superconductive Diamonds**
- **2 D Hole Gas and Surface Channel FETs with H-terminated Surface**
- **Gate oxide ⇒ Al_2O_3, higher gate-voltage-swing**
- **Mobility Improvement**
- **Carrier Transport: Velocity and Mobility Compared with SiC or GaN FETs**
- **Summary**

Diamond as wide gap semiconductor

	Si	GaAs	6H SiC	GaN	Diamond
Bandgap E_G [eV]	1.1	1.43	3.10	3.45	**5.45**
Saturated drift velocity v_S [10^7 cm/s]	1.0	1.0	2.0	2.2	**1.0 (hole)**
Carrier mobility μ [cm^2/V·s]	1500	8500	1140	1250	3800(hole)
Breakdown field E_B [MV/cm]	0.3	0.4	3	2	**~10**
Dielectric constant ε_r	11.8	12.5	9.6/10	9	5.5
Thermal conductivity λ [W/cm·K]	1.5	0.5	4.9	1.3	**22.0**
Johnson's figure of merit [10^{23} Ω·W/s^2]	2.3	9.1	910	1080	2530(hole)
Keyes' figure of merit [10^7 W/K·s]	6.7	2.0	35	10	145(hole)
Baliga's figure of merit [Si = 1]	1	48	620	24	43938 (hole)

Johnson's figure of merit
Frequency & power products
of transistors

$$JFM = \left(\frac{E_B \cdot v_S}{2\pi}\right)^2$$

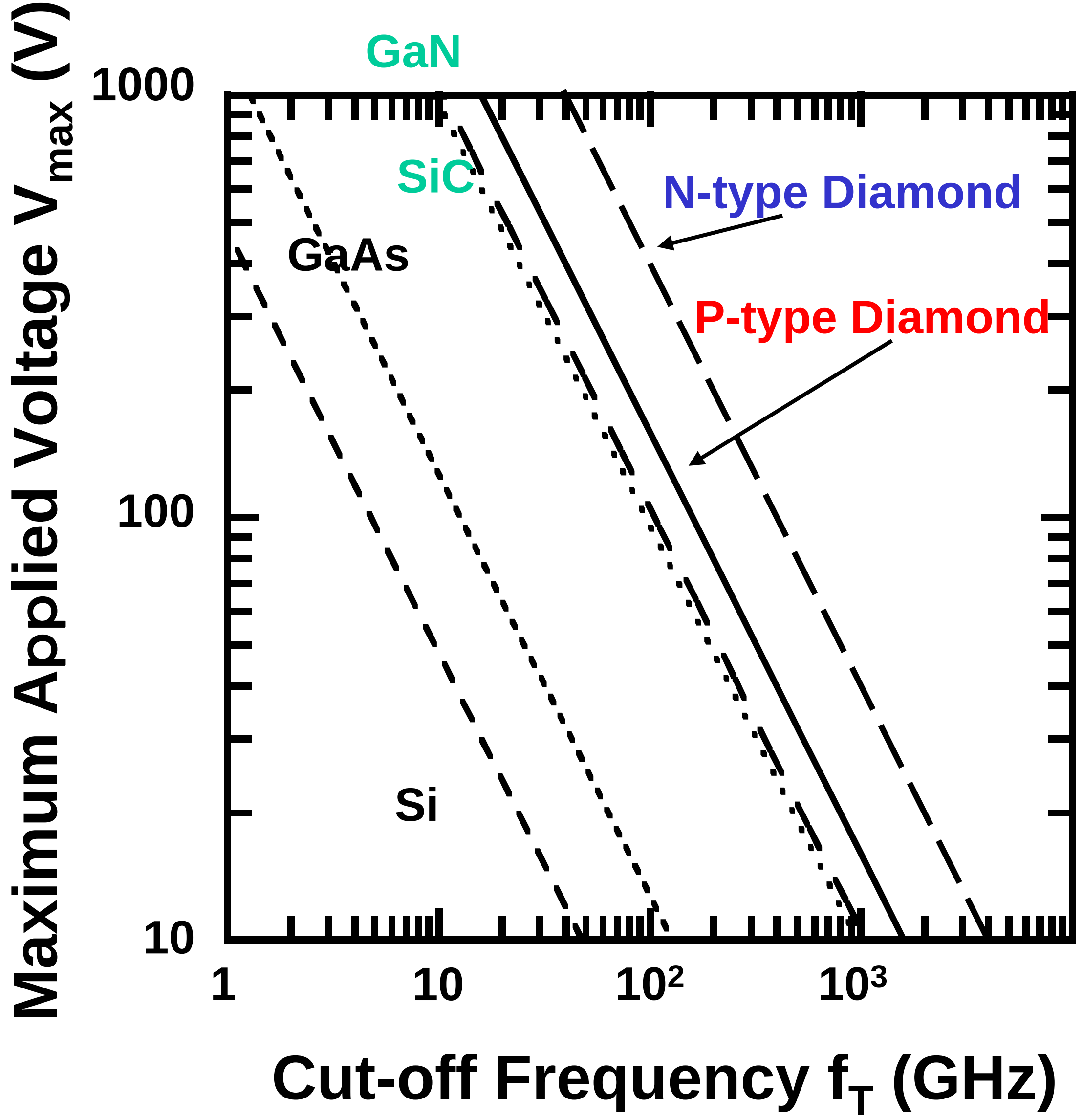
Keyes' figure of merit
Thermal limitation on
high-frequency performance

$$KFM = \lambda\left(\frac{c \cdot v_S}{2\pi \cdot \varepsilon_r}\right)^{\frac{1}{2}}$$

Baliga's figure of merit
Loss in high-power &
high-frequency operation

$$BFM = \varepsilon \cdot \mu \cdot E_B^{\,3}$$

Diamond : high power & high frequency device



Cut-off Frequency

$$f_T = \frac{v_s}{2\pi L_g}$$

vs: Saturated Velocity

P-type Diamond 10^7cm/s

Maximum Voltage

$$V_{\max} = E_b L_g$$

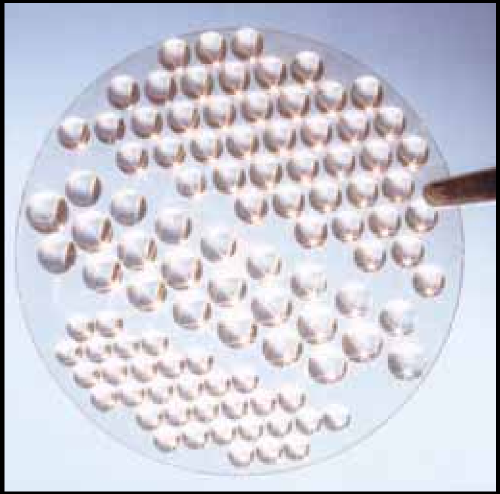
Eb: Breakdown Field

Diamond 10^7 V/cm

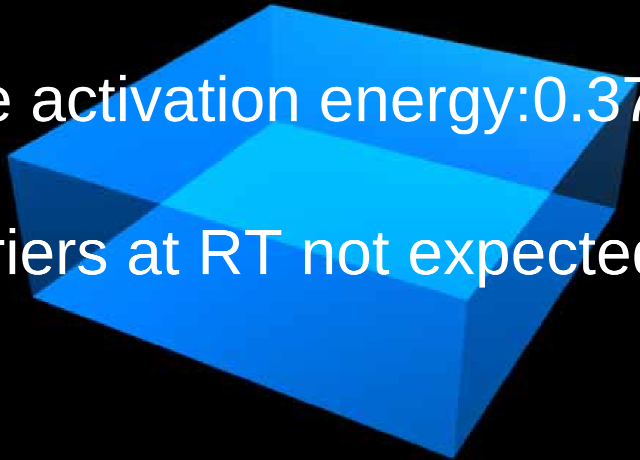
$$f_T V_{\max} = \frac{v_s E_b}{2\pi} = const.$$

Semiconducting Diamonds

Blue diamond
Hope Diamond
(Smithsonian Museum)



CVD diamond
Poly ~ ϕ150mm
Single ~ ϕ
Hetero ~ ϕ

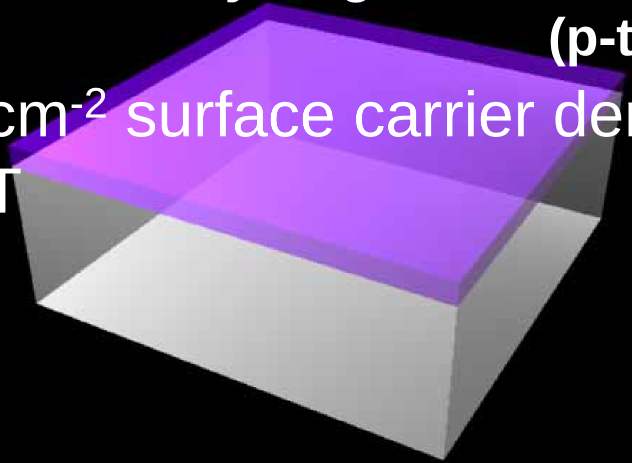


Hole activation energy:0.37eV

Carriers at RT not expected.

Boron doped diamond (p-type)

Hydrogen-termination
(p-type)

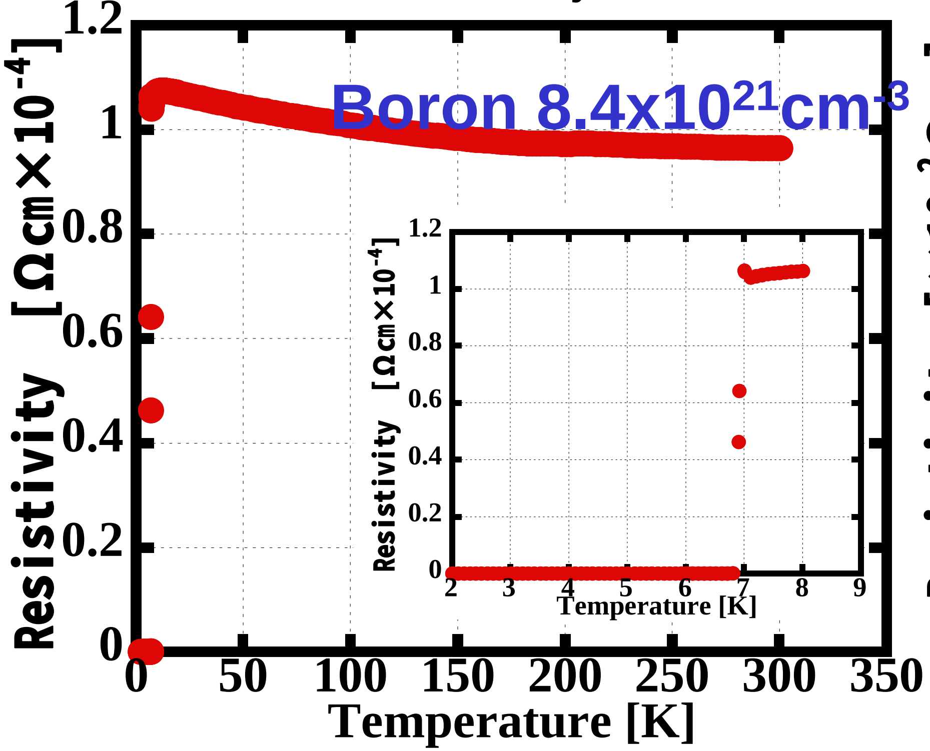


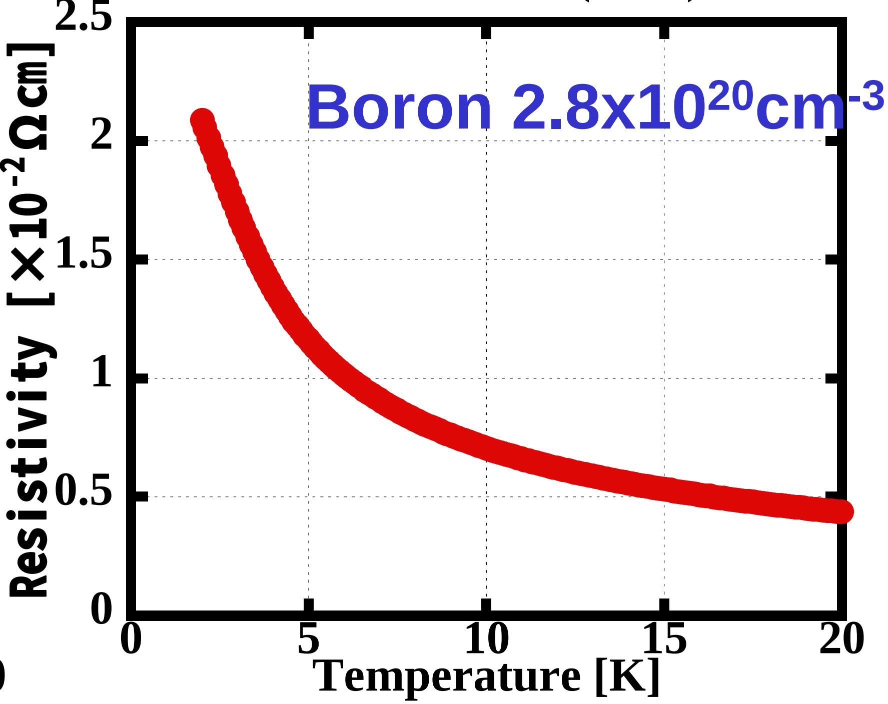
10^{13}cm^{-2} surface carrier density at RT

CVD diamond (insulating)

Superconducting diamond by boron doping

T. Yokoya, H. Kawarada, et al. Nature, 438, 647-650 (2005)



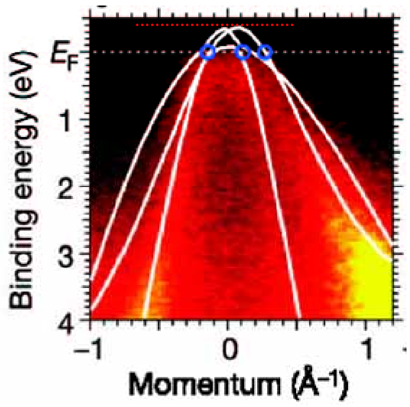


Superconductivity

Tc=7.4K

N_b=8.37×10^{21}[cm^{-3}]

N_c=1.23×10^{22}[cm^{-3}]

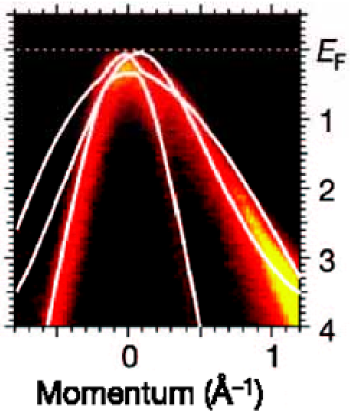


0.40 ±0.2 eV

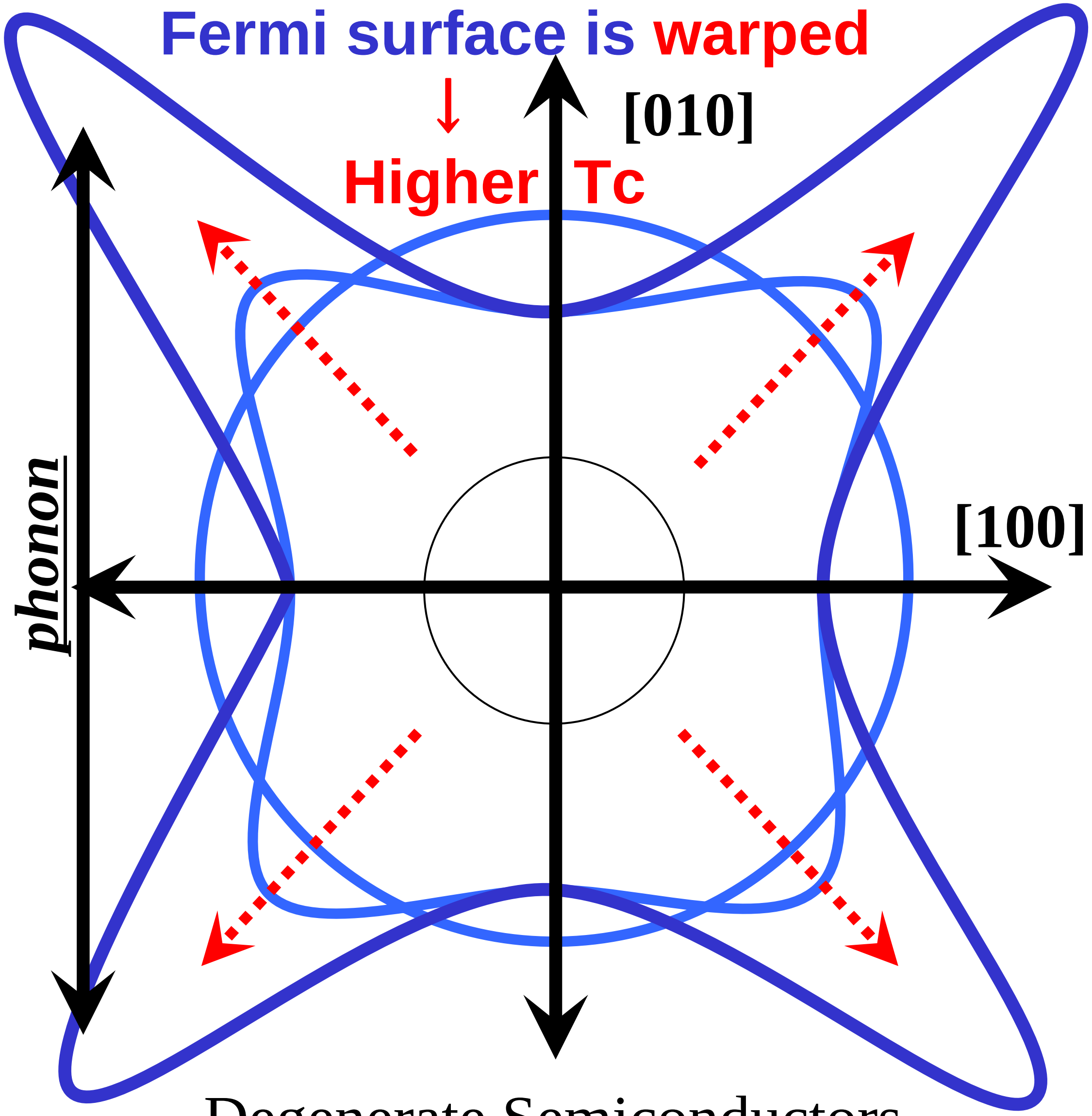
Variable Range Hopping

N_b=2.80×10^{20}[cm^{-3}]

N_c=2.92×10^{20}[cm^{-3}]



Warped Fermi Surface → Higher Tc



As Hall factor r_H decreases
Fermi surface is warped
↓
Higher Tc

Degenerate Semiconductors

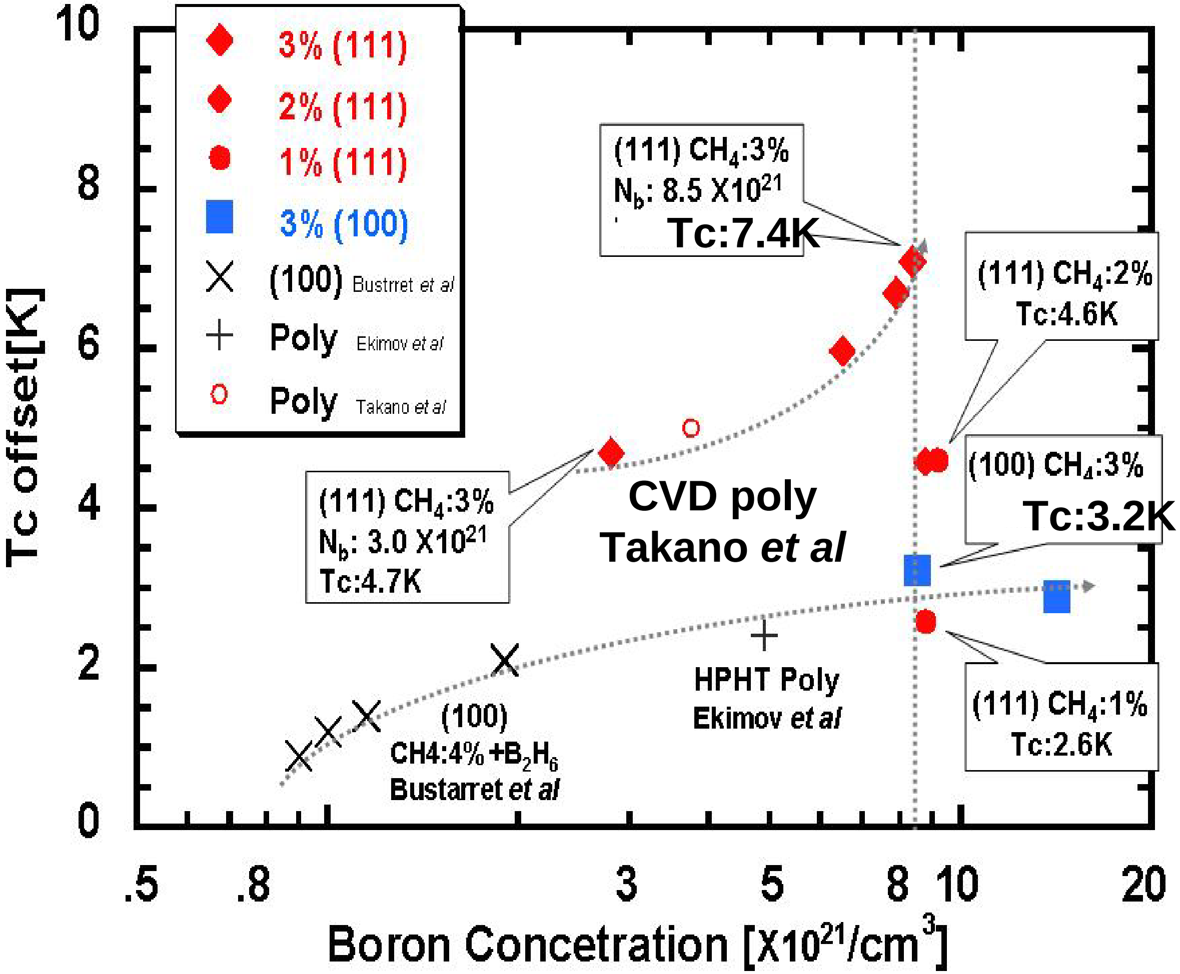
Hall factor r_H evaluation of the shape of Fermi surface

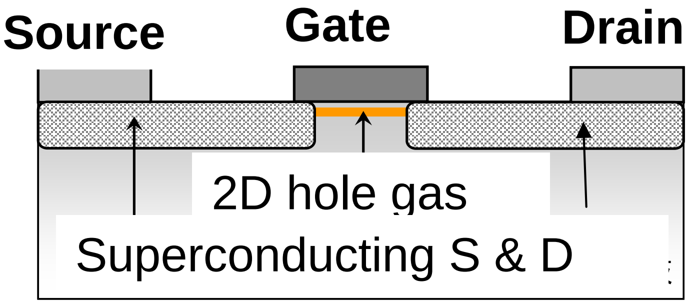
Carrier (hole) concentration is observed to be higher than acceptor (boron) concentration if we assume the Hall factor r_H is 1.

p (hole)= N_B (boron) /r_H

Estimated r_H is less than 1 and depends on Tc.
The lower r_H, the higher Tc in boron-doped diamond

Superconductivity from Tc ^{offset} by boron doped diamond and a new cryodevice

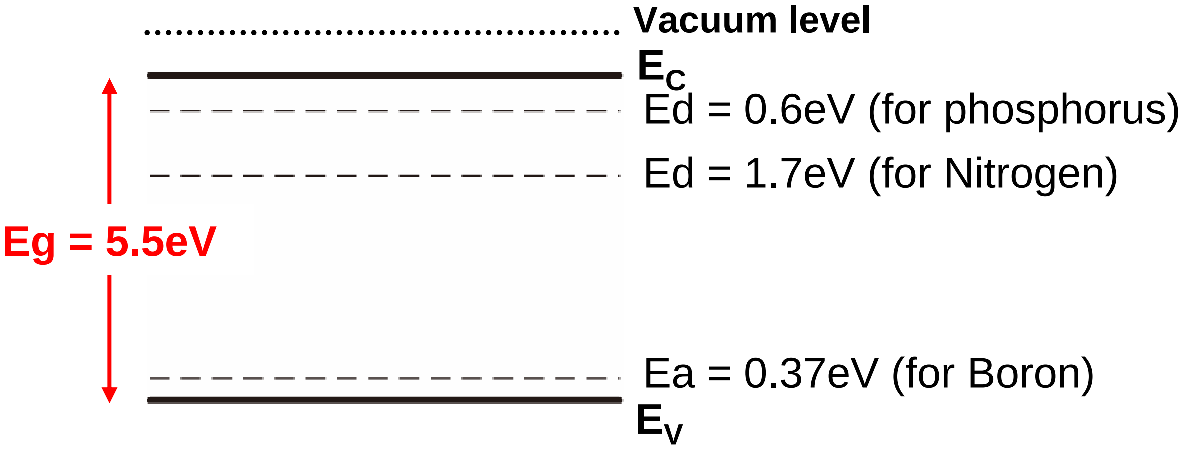




New type of cryodevice based on superconductor and semiconductor on diamond

2D hole gas transistors using diamond

◆ Device using boron-doped bulk diamond (MOS,MESFET,Bipolar)



Vacuum level

E_C

Ed = 0.6eV (for phosphorus)

Ed = 1.7eV (for Nitrogen)

Eg = 5.5eV

Ea = 0.37eV (for Boron)

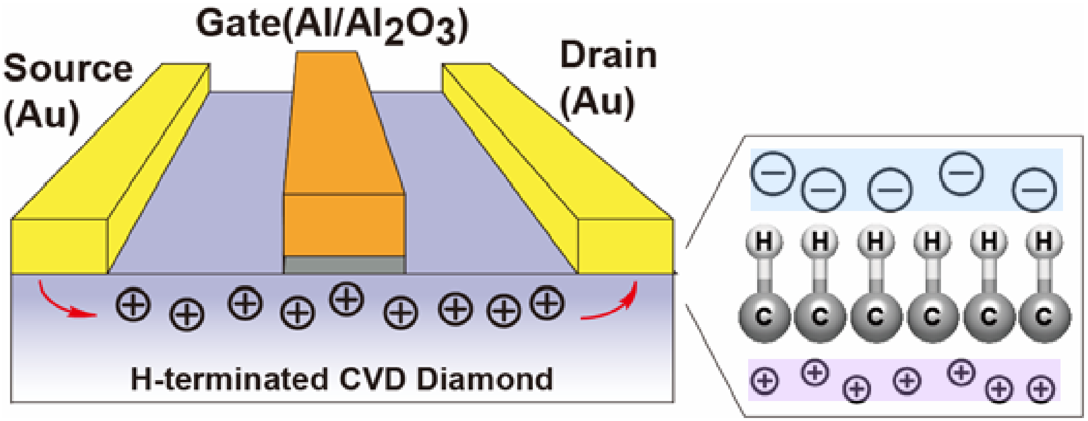
E_V

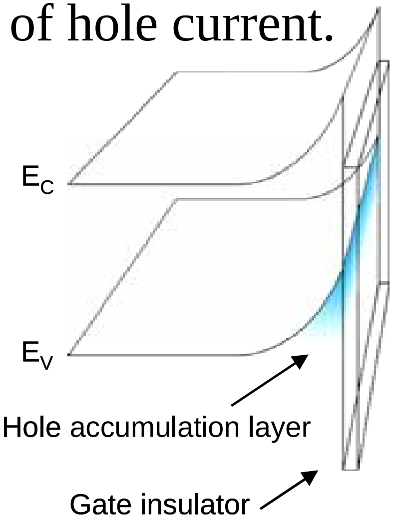
<u>High activation energies</u>

Most of impurity atoms can be hardly ionized @R.T.

◆ **Device using 2D hole gas (accumulation)** (MOSFET,MESFET)

In this device, the diamond substrate is un-doped, and the hole accumulation layer on hydrogen-terminated surface is used as a channel of hole current.

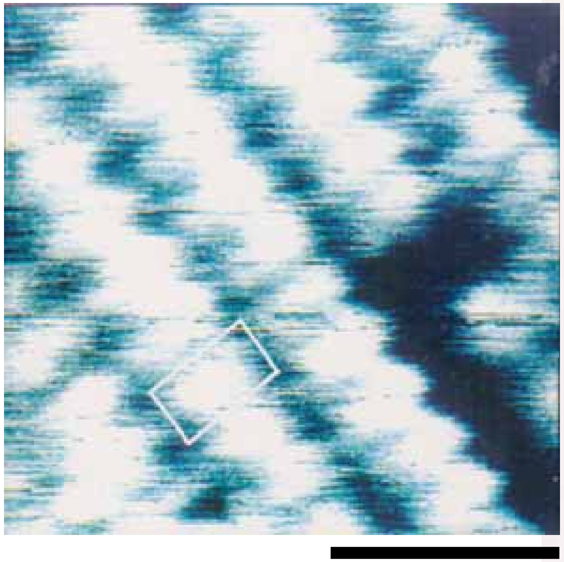




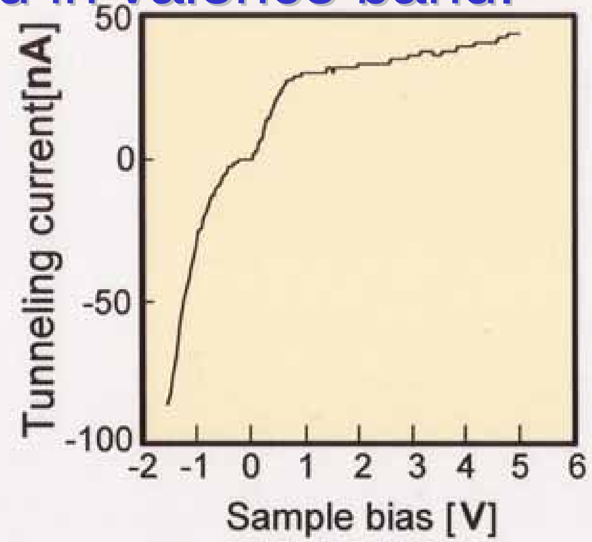
Most of diamond RF transistors have been fabricated using hole accumulation layer.

STS Spectrum of H-terminated diamond (001)

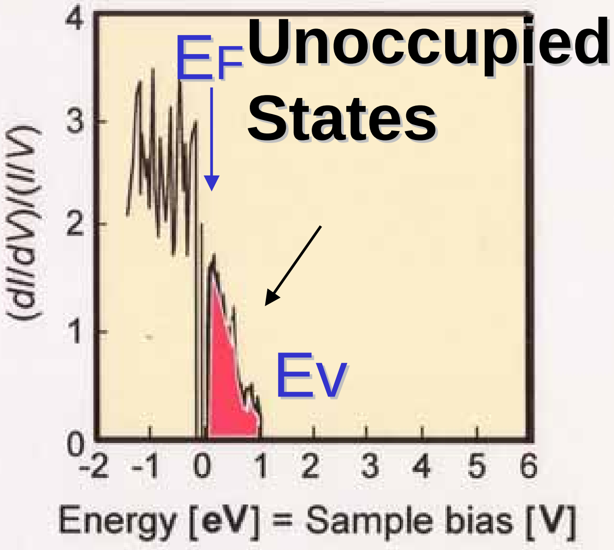
Due to high density of surface states,
Fermi level is located in valence band.



H.Kawarada et al.
Phy. Rev. B 52 (1995) 11351.



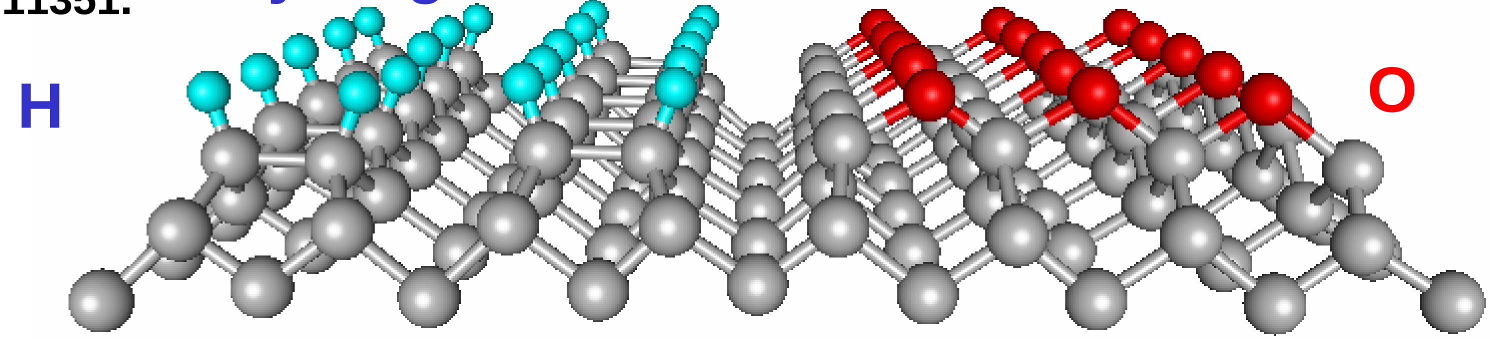
Tunneling current vs. sample bias characteristics



(dI/dV)/(I/V) vs. sample bias.

Hydrogen termination

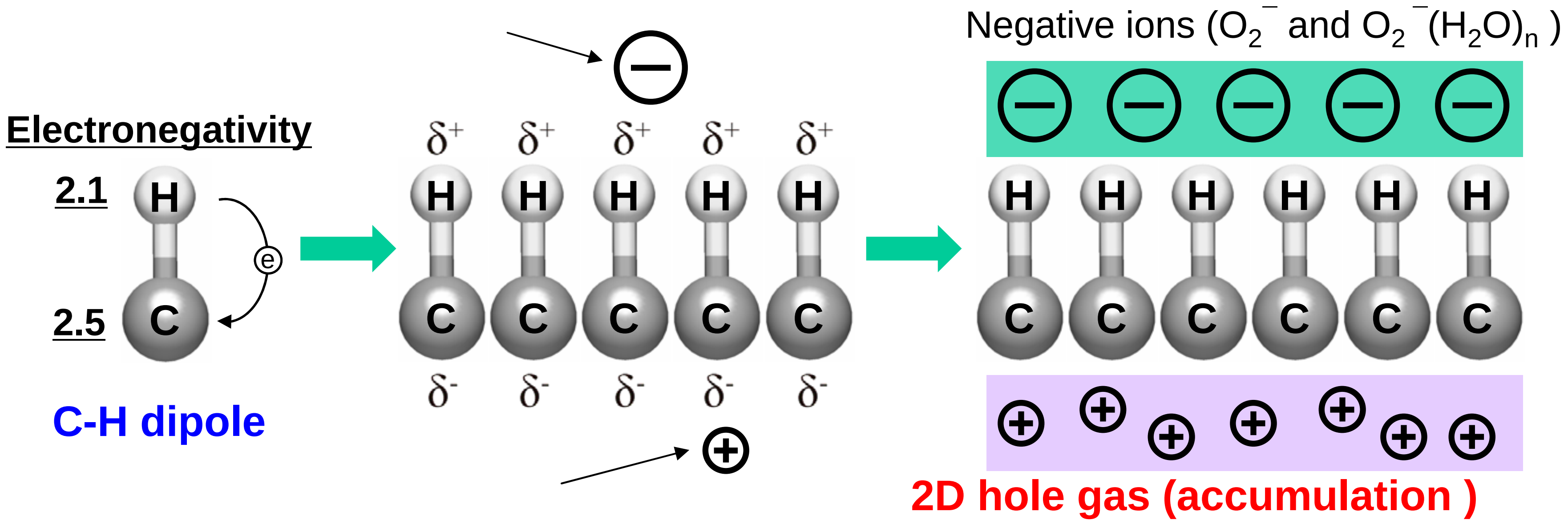
Oxygen termination

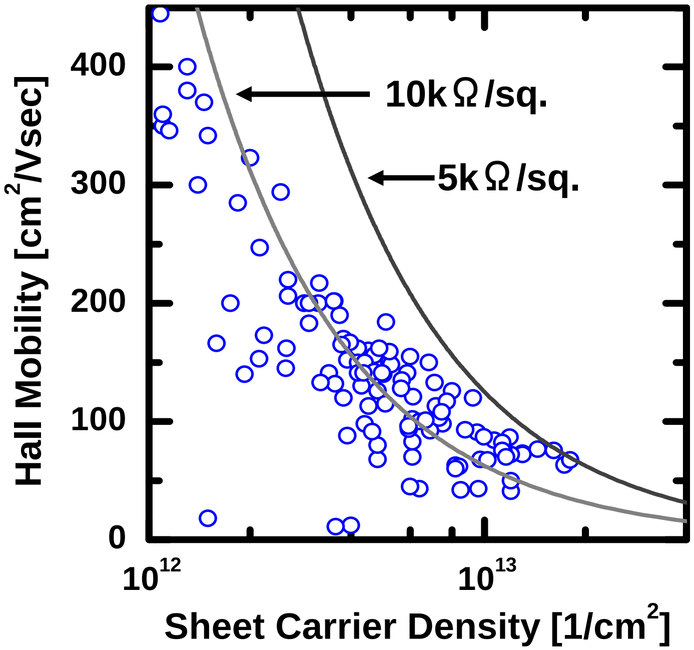


P-type（Carrier density ~10^{13} cm^{-2}）

Insulating

2D hole gas layer on hydrogen-terminated surface





Hydrogen-terminated diamond surface has **positive charge by C-H dipole**.

When the surface is exposed to air, negatively charged ions are captured by the positively charged surface.

The negatively charged ions induce upward band-bending on diamond surface.

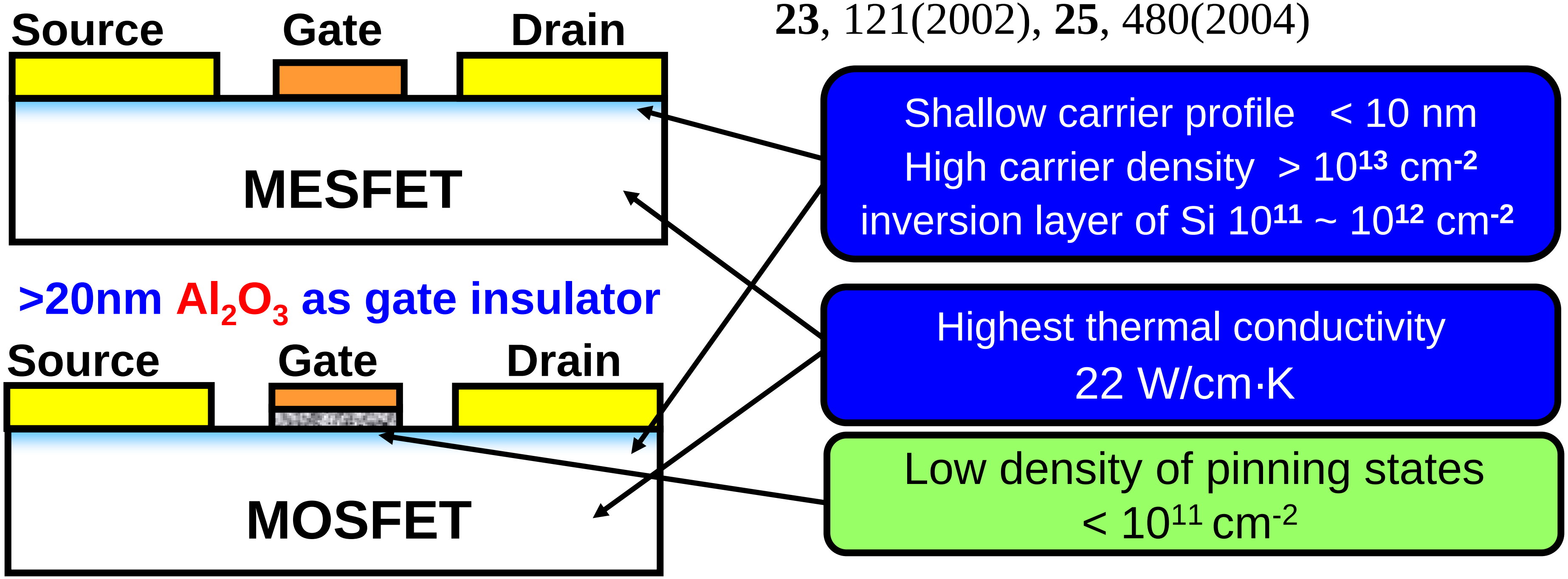
Finally, holes are accumulated on the surface to form

2 dimensional hole gas

Sheet carrier density over 10^{12} cm^{-2} can be easily obtained.

Diamond Field Effect Transistors (FETs)
MESFET and MOSFET

IEEE Elect. Dev. Lett, **22**, 390 (2001)
23, 121(2002), **25**, 480(2004)



Cu as Schottky gate electrode

>20nm Al_2O_3 as gate insulator

Shallow carrier profile < 10 nm
High carrier density > 10^{13} cm^{-2}
inversion layer of Si $10^{11} \sim 10^{12}$ cm^{-2}

Highest thermal conductivity
22 W/cm·K

Low density of pinning states
< 10^{11} cm^{-2}

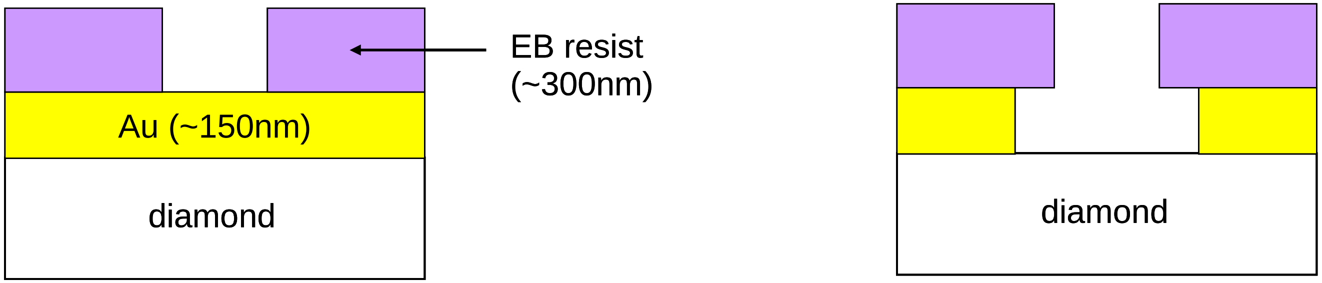
Advantages of MESFET

- **Easy to fabrication**
- **High transconductance**

Advantages of MOSFET

- **Low gate leakage current**
- **Resistant for gate enhancement**
- **Stabilization of surface conductive layer**

How to make diamond field effect transistors
Self–alignment technique

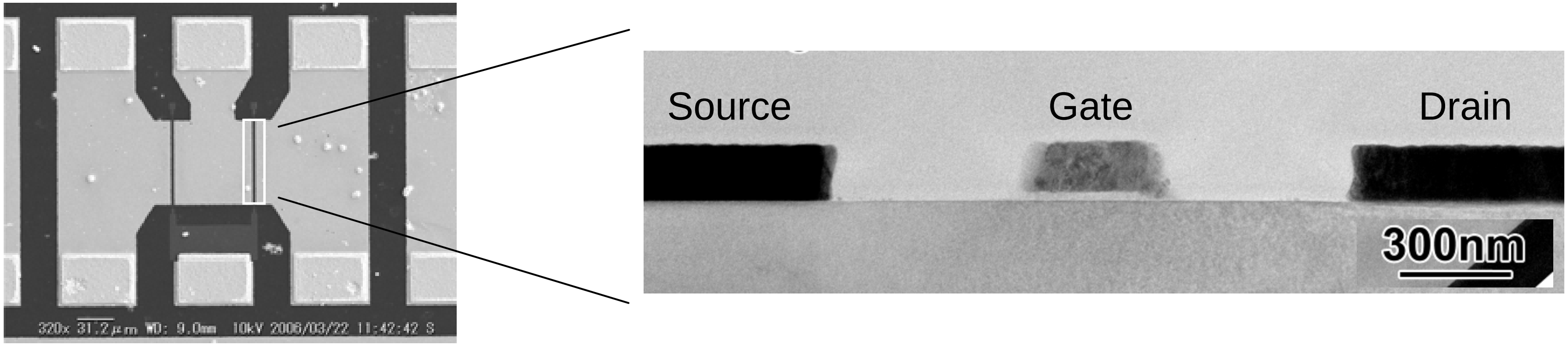


(a) EB lithography

(b) Au etching

(c) Al & Al_2O_3 deposition

(d) Lift-off



Development of Diamond RF Devices

RF Diamond MESFETs

2001 **First small signal RF measurement**

Waseda Univ., H. Taniuchi *et al.*, IEEE Electron Device Letter (EDL) 22 (2001) 390

2002 **First RF power measurement**

Ulm Univ., A.Aleksov *et al*. Device Research Conference proceedings (2002) 181

2004 **First Noise Figure measurement**

f_T : 24.6GHz and f_{max} : 80GHz

Ulm Univ. and NTT BRL, M. Kubovic *et al.*, DRM 13 (2004) 802

2005 **2W/mm output power @ 1GHz**

NTT BRL, M. Kasu *et al.*, Electronics Letter, 41 (2005) 22

2006 **f_T : 45GHz and f_{max} : 120GHz**

NTT BRL, M. Kasu *et al.*, IEEE EDL, 27 (2006) 570

RF Diamond MOSFETs

2002 **First small signal RF measurement**

Waseda Univ., H. Umezawa *et al*. IEEE EDL 23 (2002) 121

2004 **f_T : 23GHz**

Waseda Univ., H. Matsudaira *et al.*, IEEE EDL 25 (2004) 408

2006 **Highest f_T of 30GHz for single crystal diamond FETs**

Waseda Univ., K. Hirama *et al.*, IEEE nternational Symposium on Power Semiconductor Devices and ICs (ISPSD) proceedings (2006) 49

2007 **Highest f_T of 45GHz for diamond FETs**

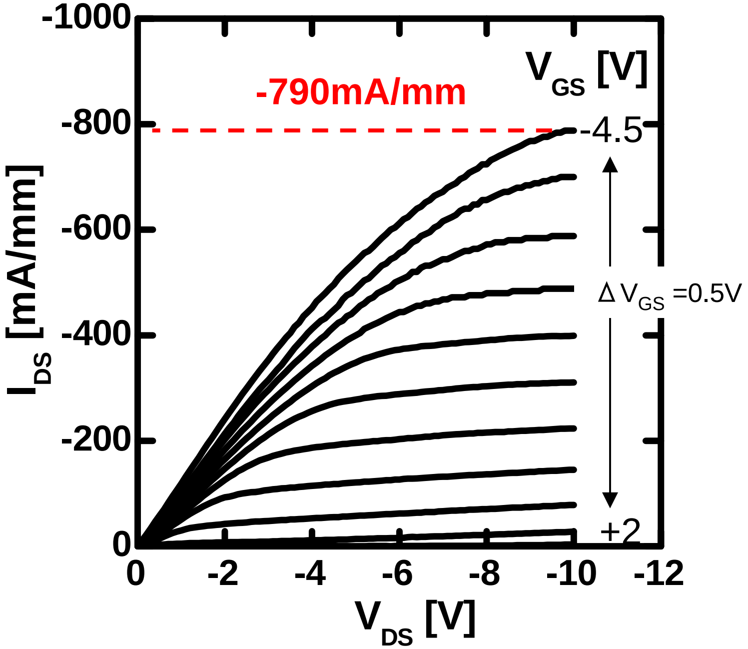
Highest I_{DS} of -790mA/mm

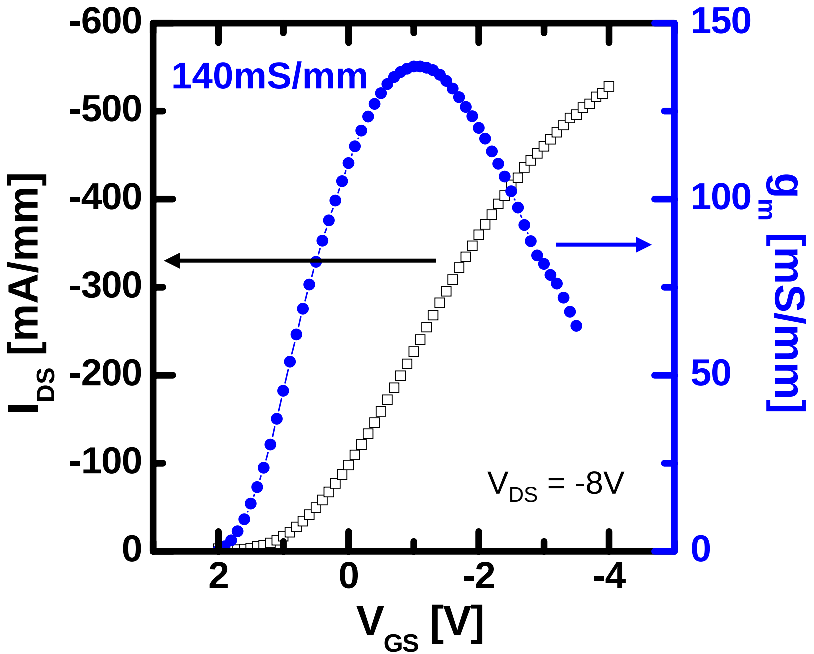
Waseda Univ., K. Hirama *et al.*, IEEE ISPSD proceedings (2007) 269

Waseda univ. fabricated RF diamond MES and MISFETs for the first time, and has improved MISFETs.

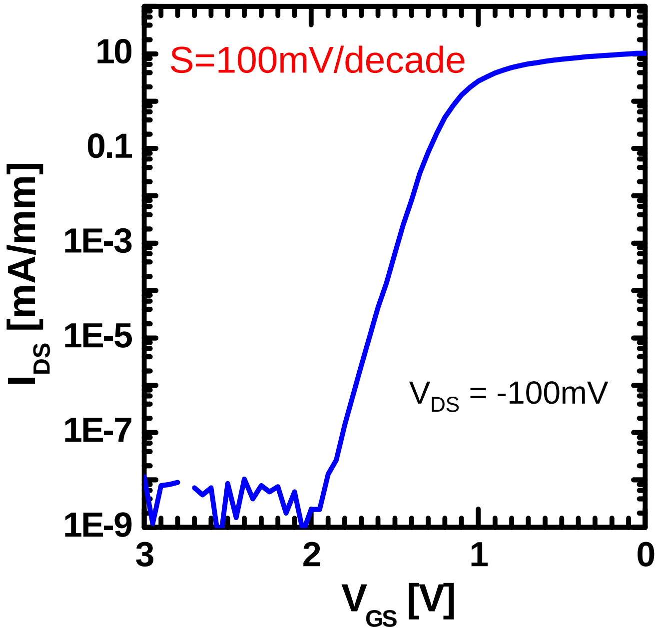
Ulm univ. and NTT BRL have improved MESFETs and demonstrated power characteristics for the first time.

0.25µm-gate-length MOSFET





Normally-on operation



Gate length:0.25µm

Gate width:25µm

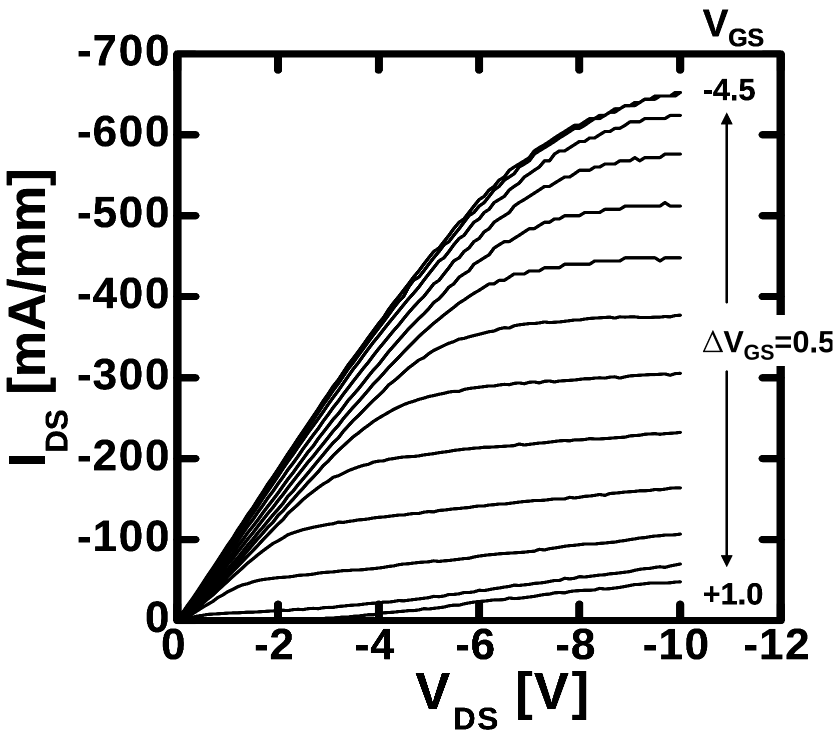
Maximum drain current:-790mA/mm

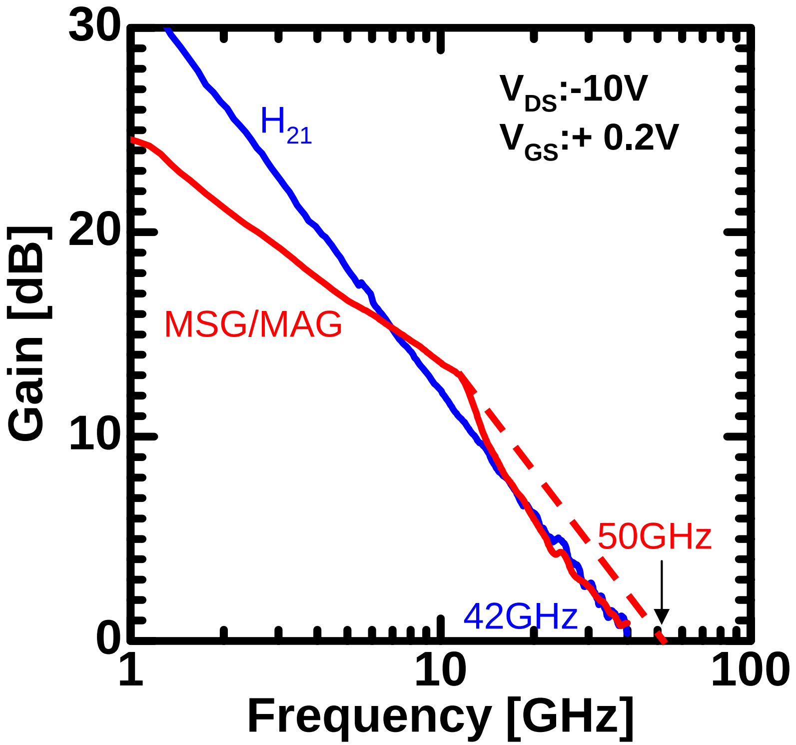
Maximum g_m:140mS/mm

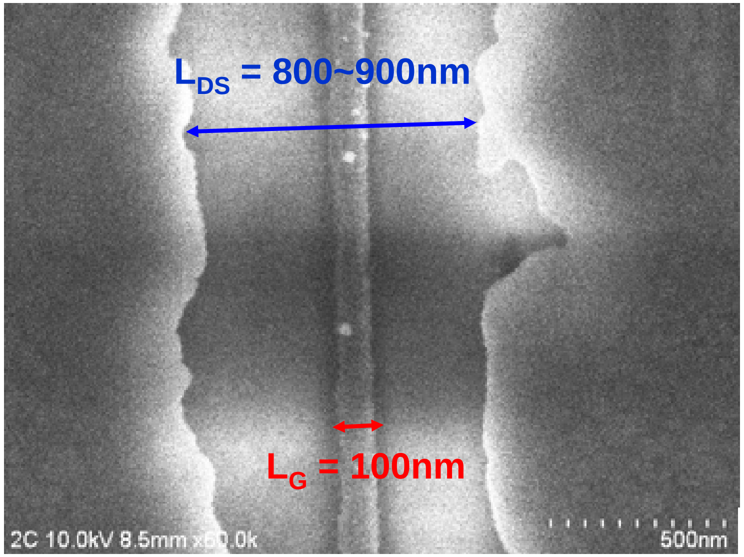
Subthreshold factor:100mV/decade

The I_{DS} of **790mA/mm** is **the highest value** for diamond FETs.

0.1μm-gate-length MOSFET







Gate length:0.1μm

Gate width:25μm

Maximum drain current:-650mA/mm

f_T:42GHz

Mason's U: 50GHz

Al_2O_3 Gate Insulator

Gate Leakage Characteristic

GaN MISFET

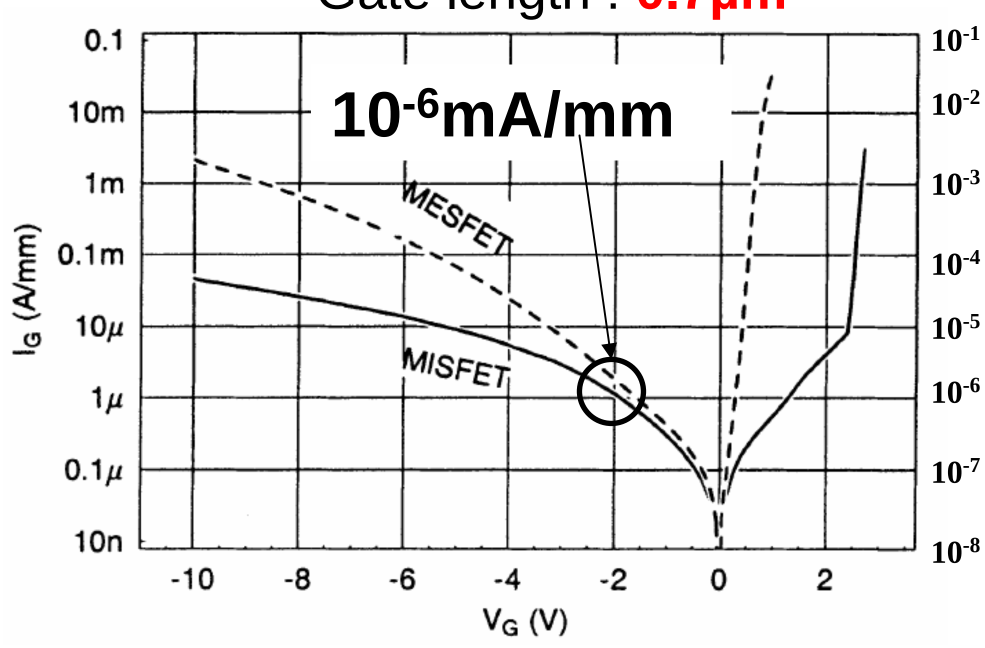
SiN thickness : **4nm**

Gate length : **0.7μm**

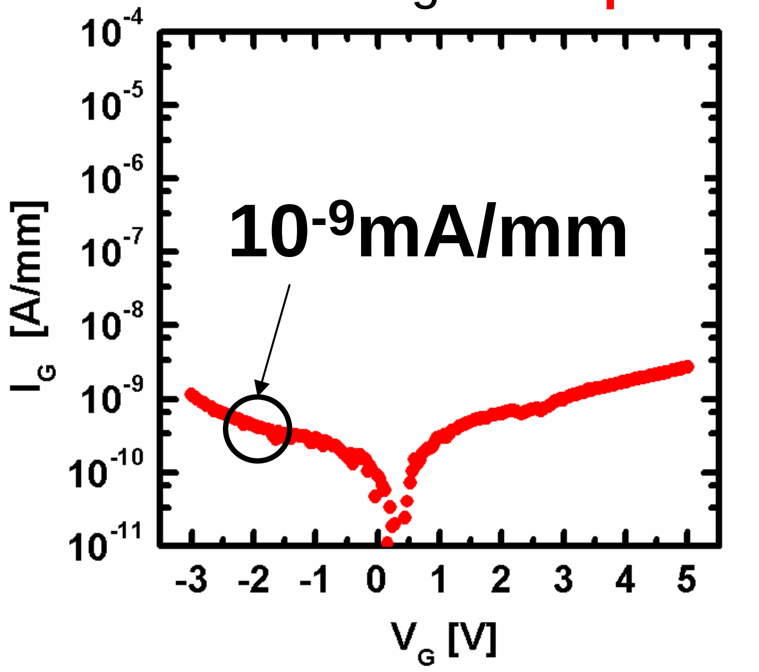
Diamond MOSFET

Al_2O_3 thickness : **3nm**

Gate length : **0.4μm**



A.Chini et al. (IEEE EDL Vol.25 No.2 2004)



Using Al_2O_3 as gate insulator, gate leakage of Diamond MOSFET was three digit lower than SiN gate insulator GaN MISFET

Cut off frequency and velocity

IEEE Elect. Dev. Lett, **22**, 390 (2001)
23, 121(2002), **25**, 480(2004)

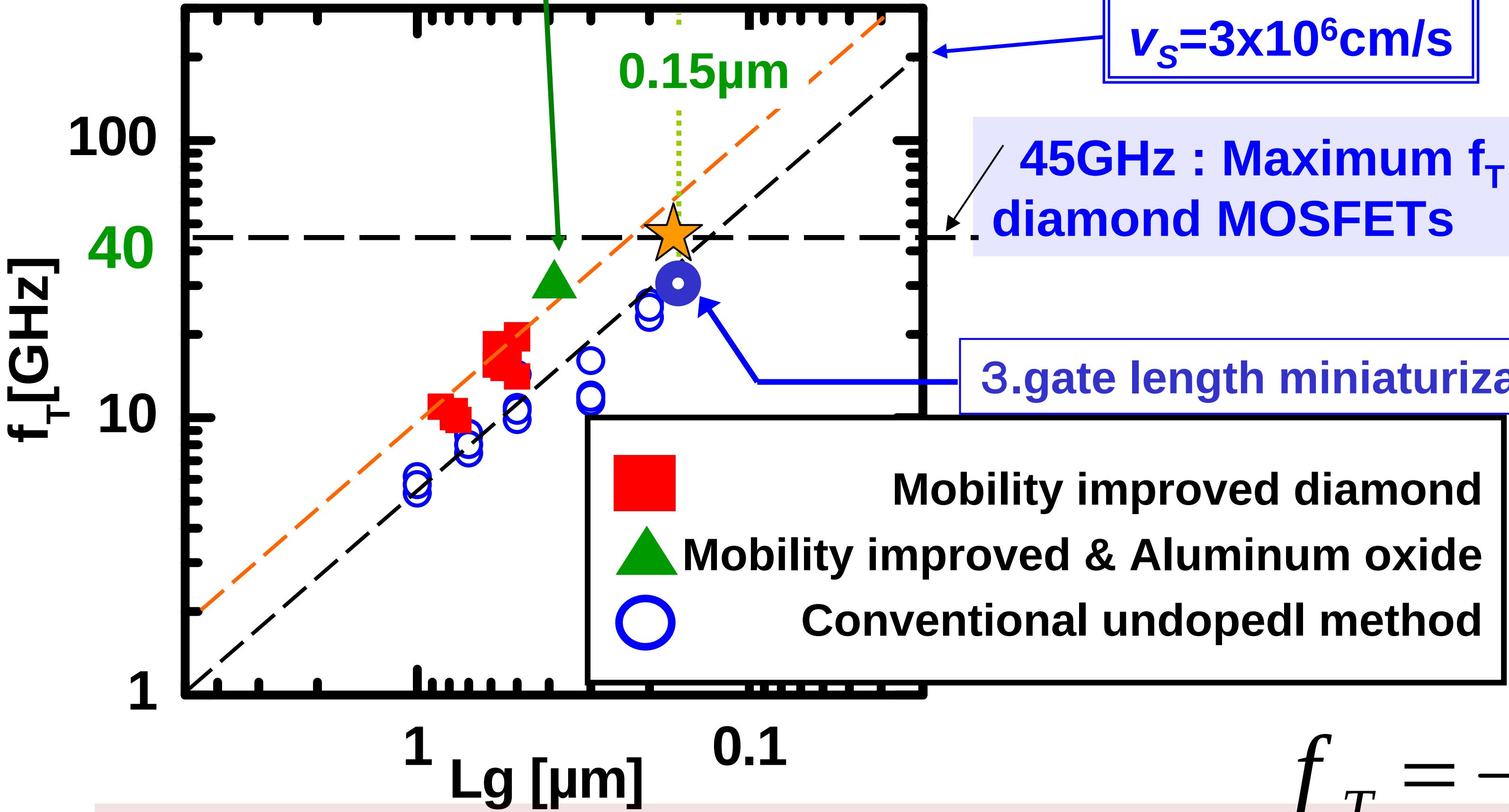
1. high channel mobility
&
2. Al2O3 gate insulator

v_S=6x10^6cm/s

v_S=3x10^6cm/s

45GHz : Maximum f_T for diamond MOSFETs

3.gate length miniaturization

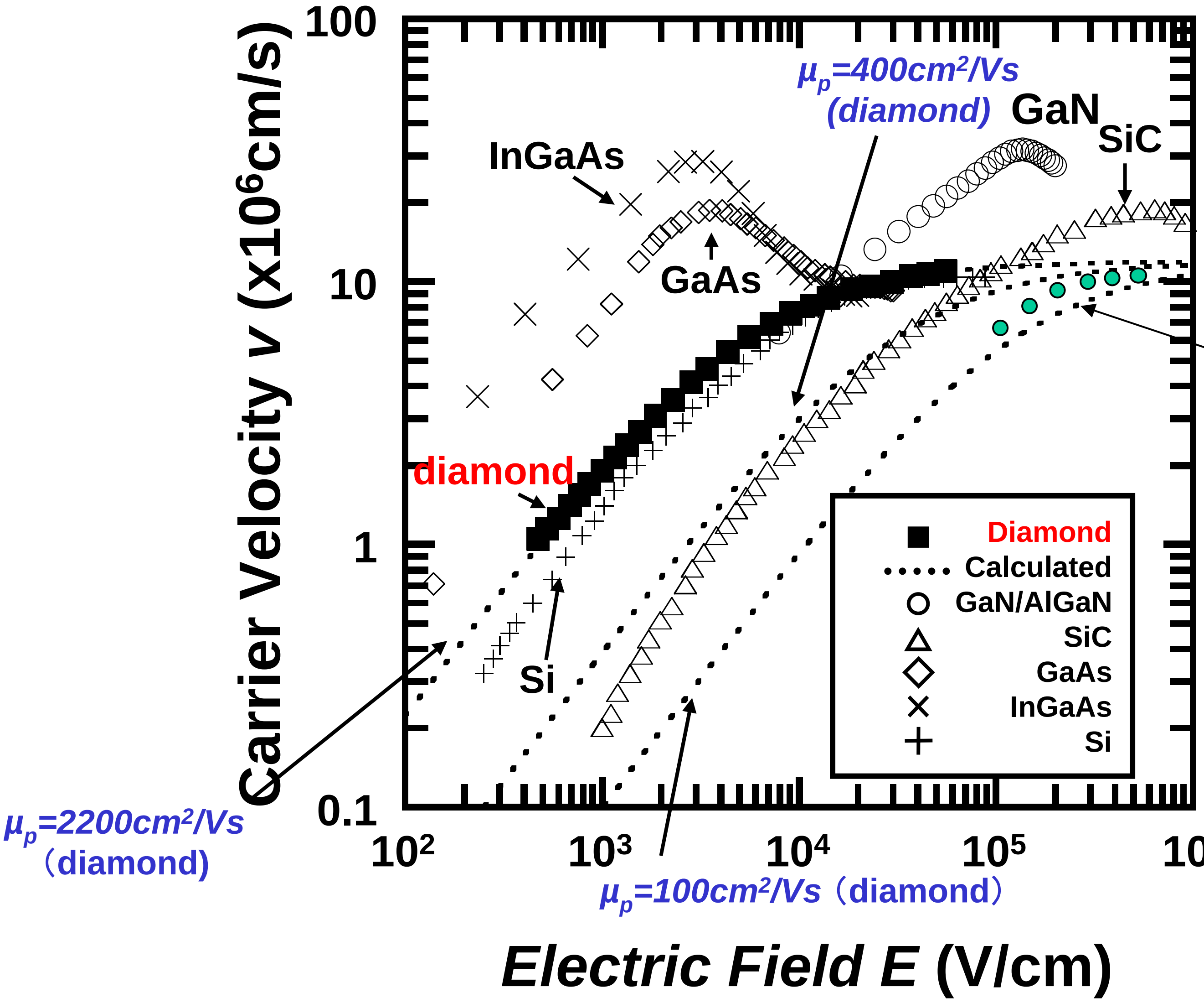


$$f_T = \frac{v_s}{2\pi L_g}$$

★ High channel mobility, Al_2O_3 gate insulator,
gate length miniaturization → f_T = 42GHz

Diamond transistors operated at high Electric Field

Carrier Velocity dependence on Electric Field

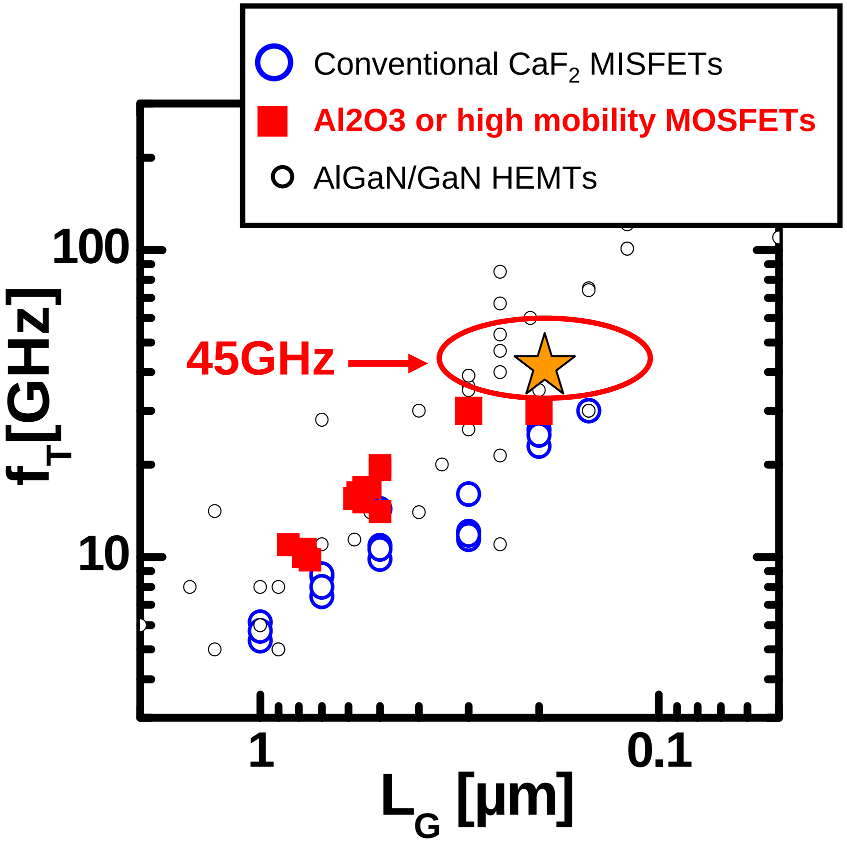


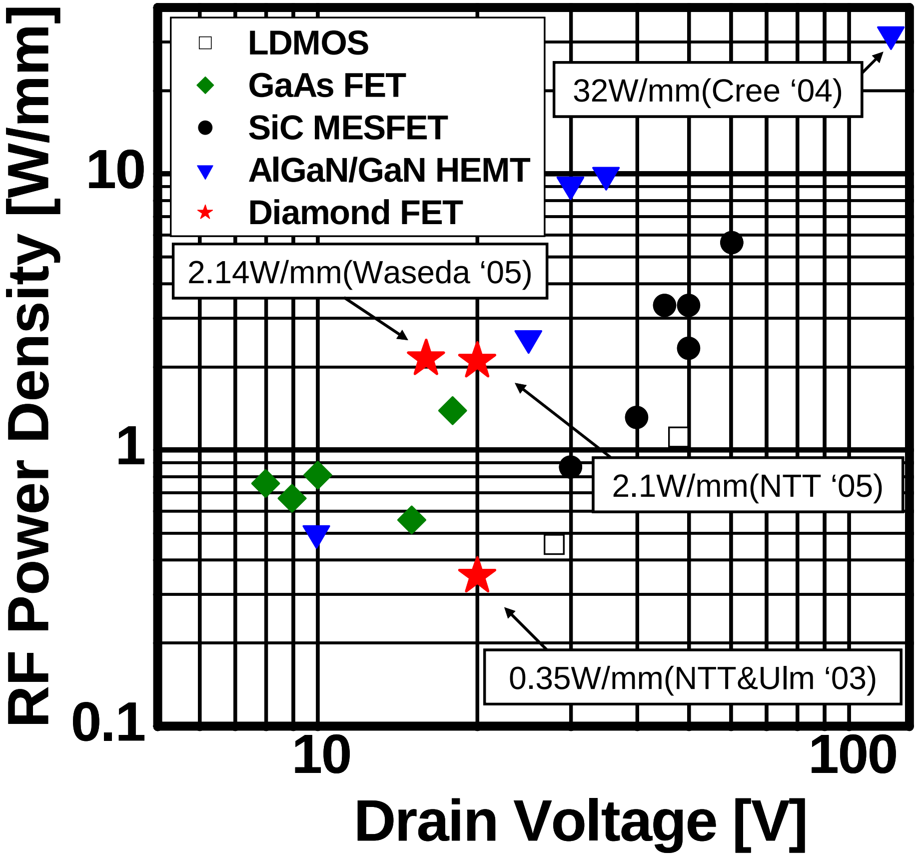
0.1-0.2 μm Gate Diamond FET

Channel Mobility $100-200\ cm^2/Vs$ at RF Operation

RF performance comparable with AlGaN/GaN

Compared with Si, GaAs, SiC, AlGaN/GaN, diamond FETs shows comparable or better device performance.



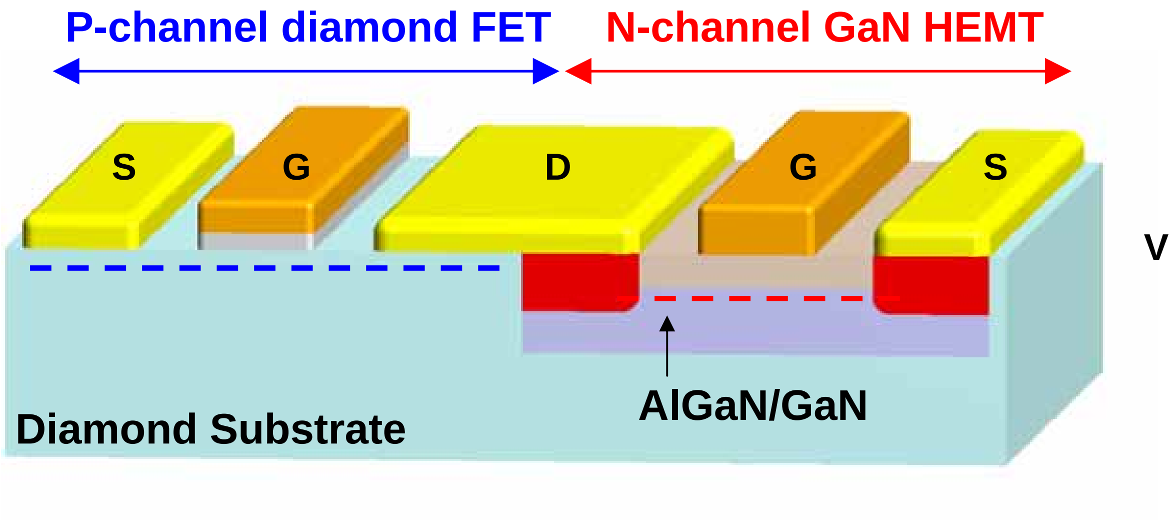


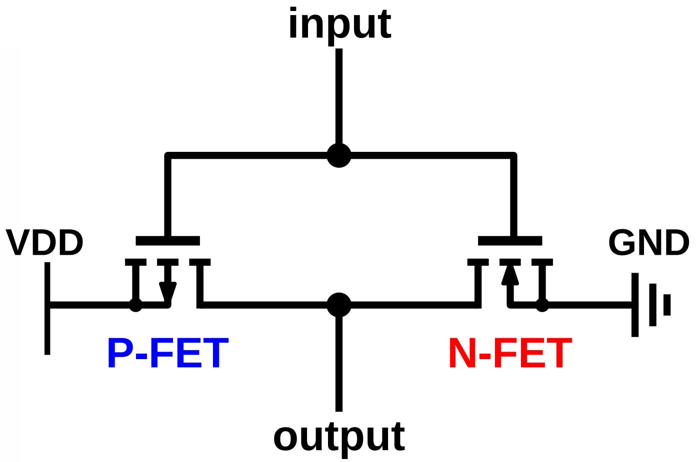
The f_T of 45 GHz is higher than that of SiC MESFETs

The RF power densities of diamond FETs have exceeded those of Si LDMOSFET and GaAs FETs.

Diamond coexists with AlGaN/GaN

DC and RF performance of p-channel diamond FETs is steady improving and approaching GaN HEMTs.





high power RF complementary device.

High diamond thermal conductivity can suppress the self-heating of high power devices.

Complementary devices have a wide range of application.

- mixer
- voltage-controlled oscillator
- high efficiency power amplifier (D,E class)

Summary I

- **Highly boron doped diamond exhibits superconductivity below 7K. Coexistence of Super- and Semiconductivity.**
- **The 2D hole gas (hole accumulation) can be caused by spontaneous polarization by H-termination. The surface stabilization might be carried out by passivation.**
- **Diamond MOSFET using aluminum oxide as gate insulator.**
- **Maximum cut-off frequency is ~50GHz. The estimated hole velocity is 6×10^{6} cm/s, which is a half of saturated hole velocity. The channel mobility at RF operation is evaluated to be 100-200 cm^{2}/Vs .**
- **The output power density exceeds that of Si LDMOS and GaAs MESFET.**
- **The best p-channel FET by diamond can coexist with the best n-channel FET by AlGaN/GaN.**

Outline for subject 3

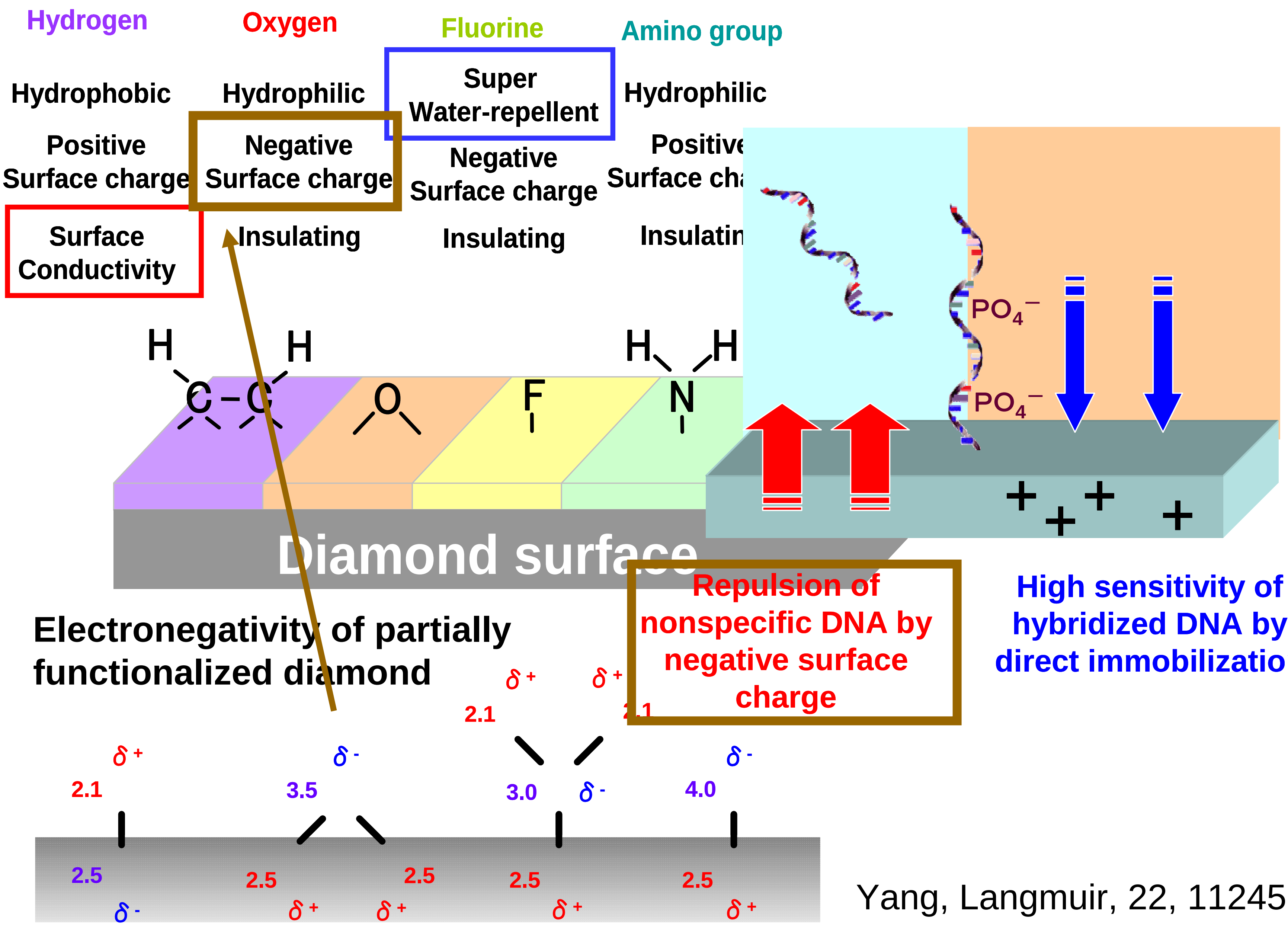
- Why diamond for DNA sensor?
- DNA immobilization on modified diamond surfaces
- Diamond electrolyte solution-gate Field Effect Transistors (SGFETs)

  different from conventional Si ISFET
- DNA hybridization detection in static and real time
- Mismatch detection

  1 base mismatch detection can be realible

Summary

DNA Repulsion by Surface Negative Charge



Hydrogen	**Oxygen**	**Fluorine**	**Amino group**
Hydrophobic	**Hydrophilic**	**Super Water-repellent**	**Hydrophilic**
Positive Surface charge	**Negative Surface charge**	**Negative Surface charge**	**Positive Surface cha**
Surface Conductivity	**Insulating**	**Insulating**	**Insulatin**

Repulsion of nonspecific DNA by negative surface charge

High sensitivity of hybridized DNA by direct immobilization

Electronegativity of partially functionalized diamond

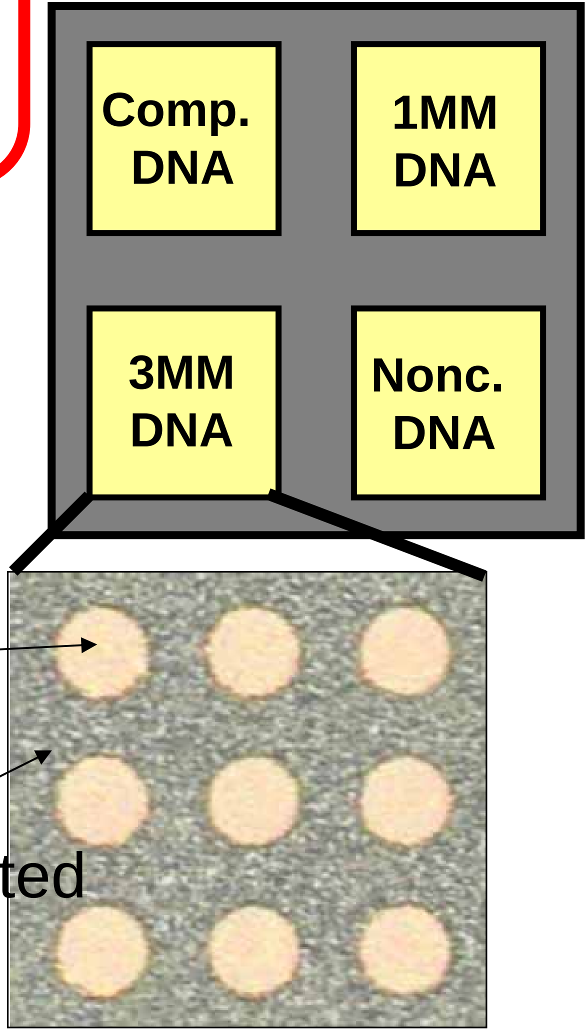
Yang, Langmuir, 22, 11245 (2006).

Direct immobilization of carboxylated probe DNA

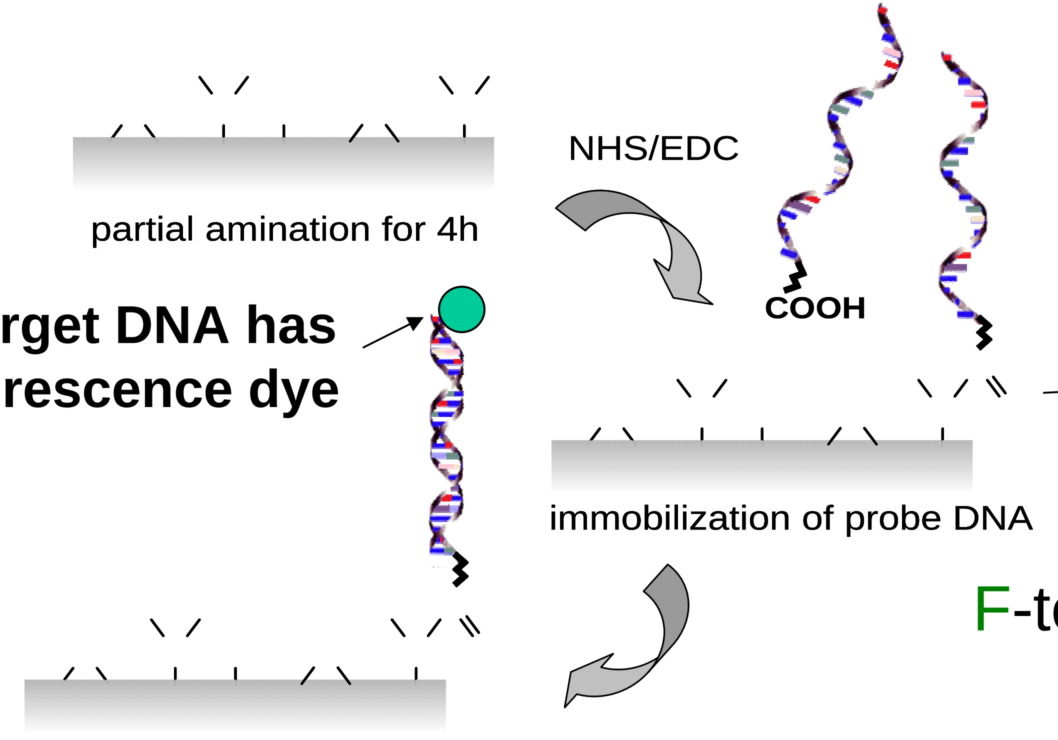
Used DNA sequence

Target. DNA:Cy5 3’-GGTGCCTGATGAAGTTTTGAT-5
Comp. probe DNA: HOOC-5'-CCACGGACTACTTCAAAACTA-3’
1MM probe DNA: HOOC-5'-CCACGGACTAGTTCAAAACTA-3’
3MM probe DNA: HOOC-5'-CCAGGGACTAGTTCAATACTA-3’
Noncomp. probeDNA:HOOC-5'-ATCGATCGATCGATCGATCGA-3'

Micropatterned Diamond



Direct immobilization of DNA on functionalized diamond



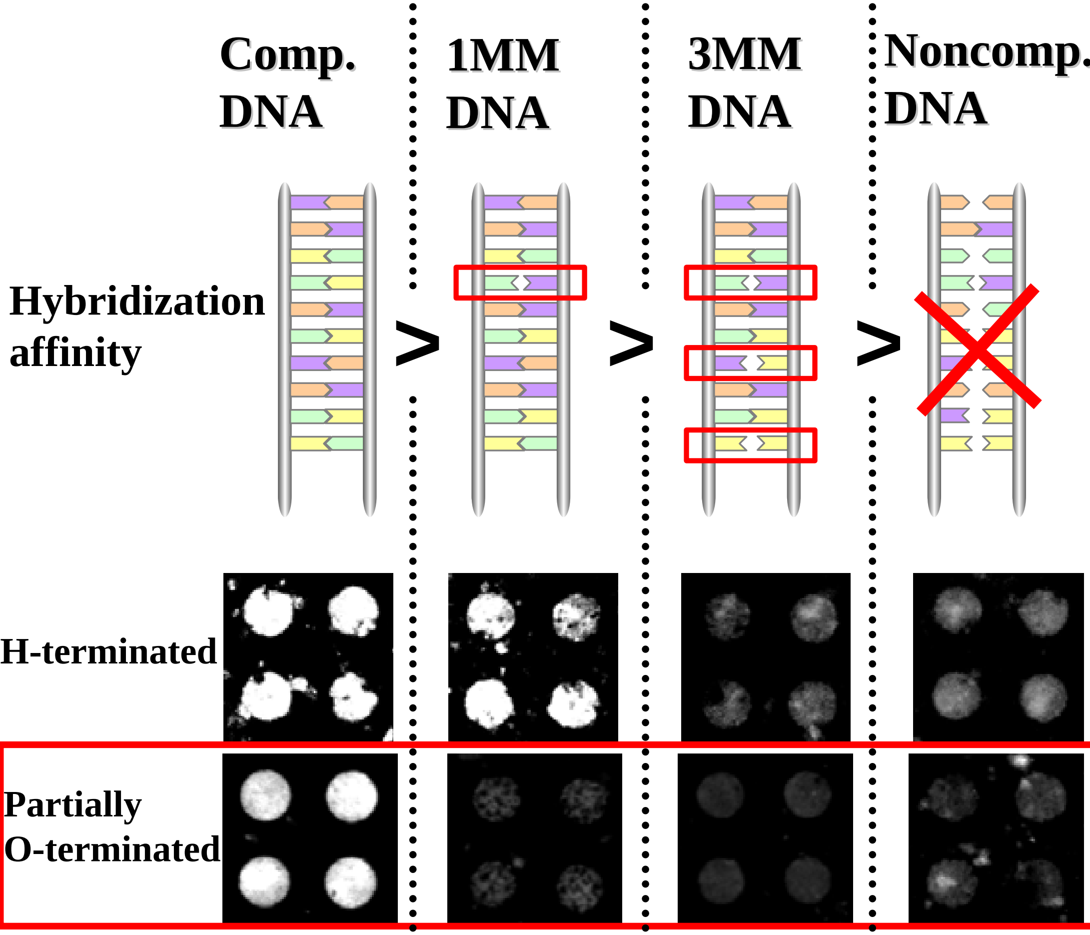
Target DNA has florescence dye

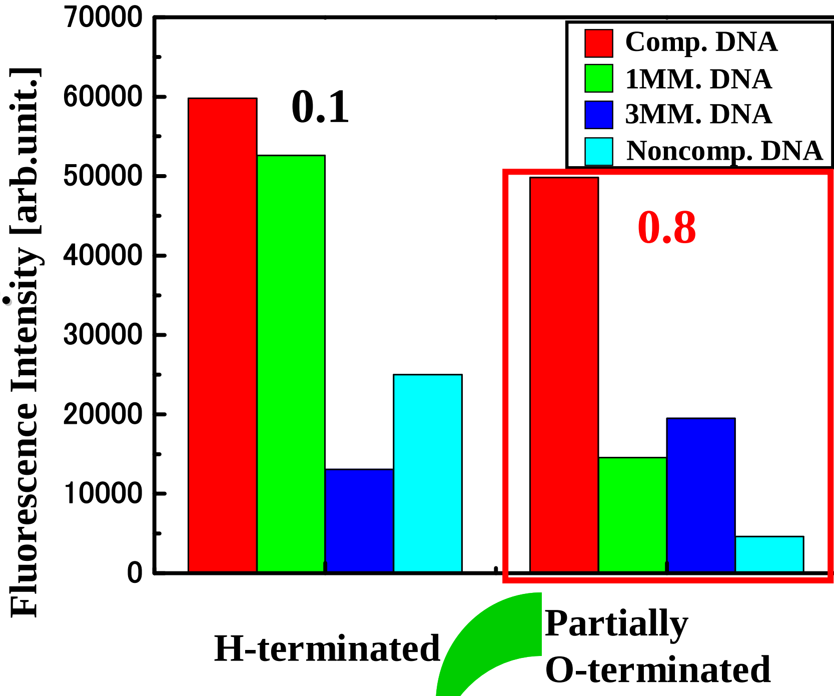
Yang, Kawarada et al. (submitted)

1 base mismatch detection by florescence

Yang, Kawarada et al. (submitted)

Target DNA conc. 100nM
in 2×SSC buffer solution
Hybridization temp. 55℃
Hybridization time 30min

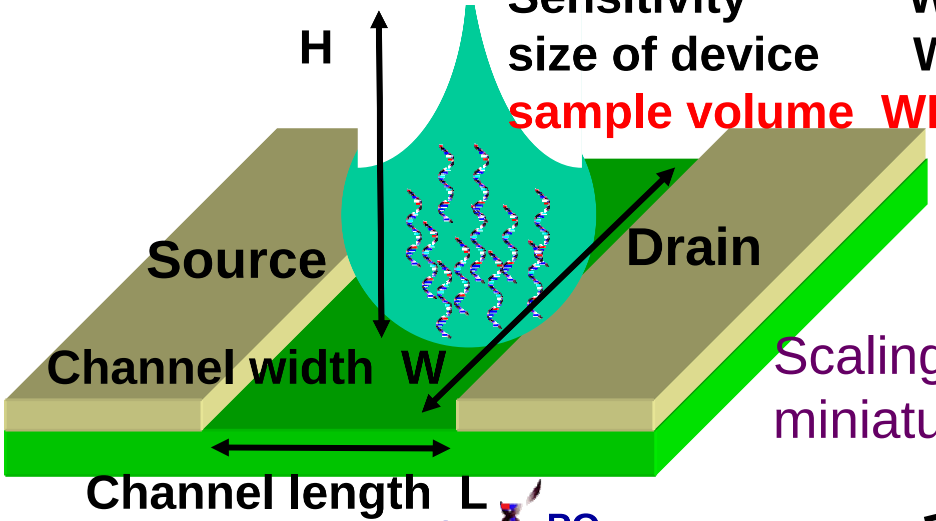




High Contrast

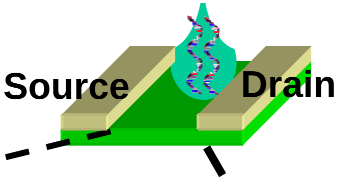
Used for FET Detection

Advantages of diamond electrolyte solution gate FET (SGFET) compared with Si ion sensitive FET



Sensitivity	W/L	1	sensitivity	1
size of device	WL	1	chip size	$1/k^2$
sample volume	WLH	1	sample volume	$1/k^2 \sim 1/k^3$

Miniaturized DNA-Sensor

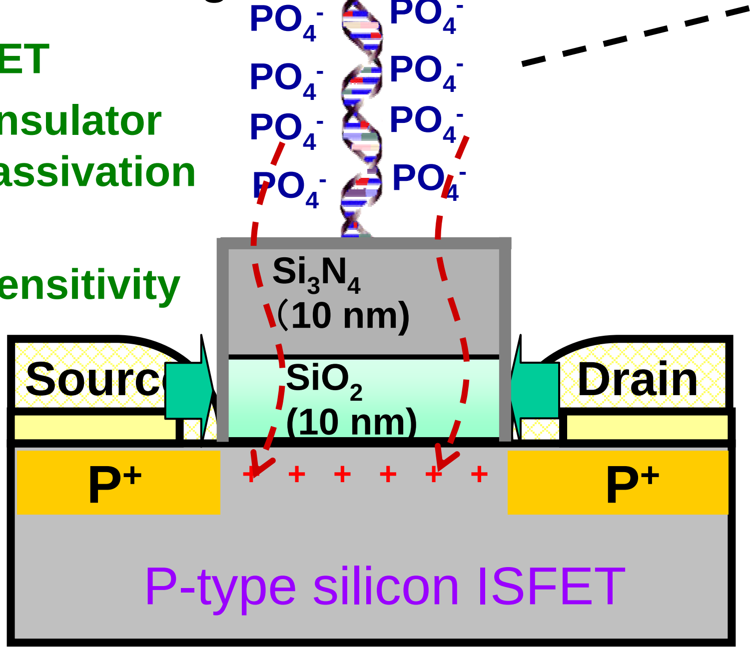


Scaling rule of transistor miniaturization：1/k

Si-ISFET

Gate insulator and passivation layers

Low sensitivity

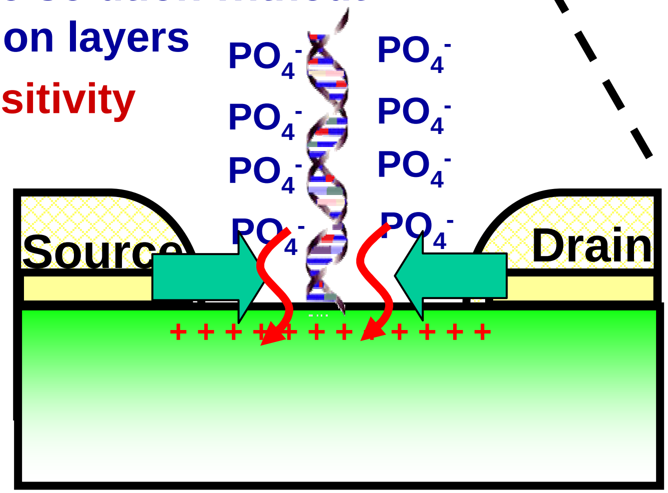


P-type silicon ISFET

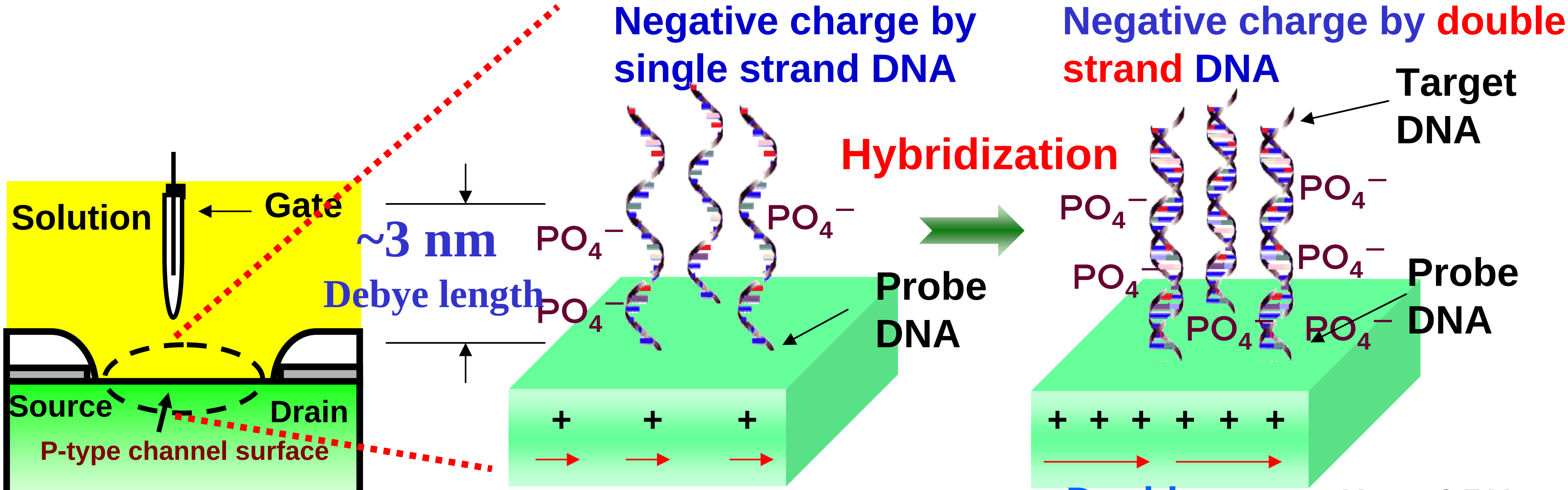
Diamond SGFET

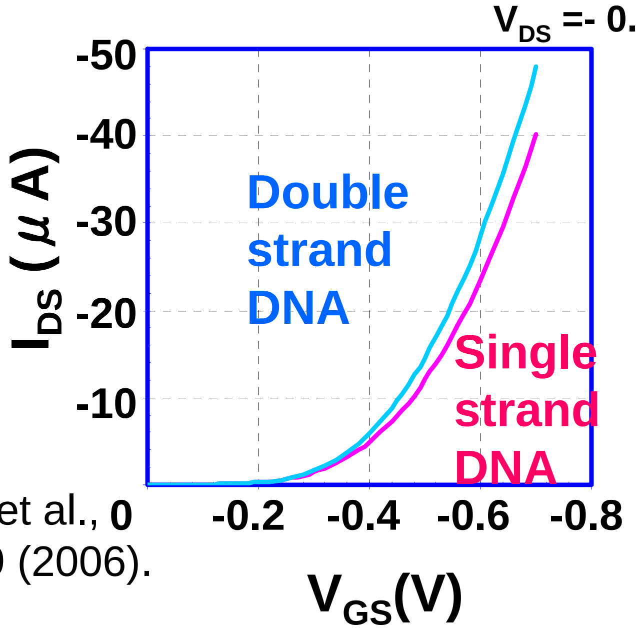
Directly exposed channel surface to solution without passivation layers

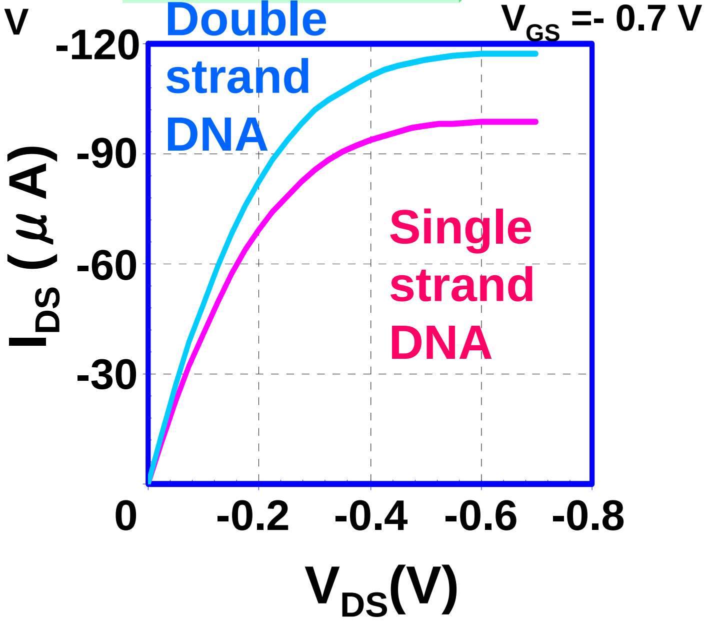
High sensitivity



Holes are induced by intrinsic negative charge of DNA after hybridization





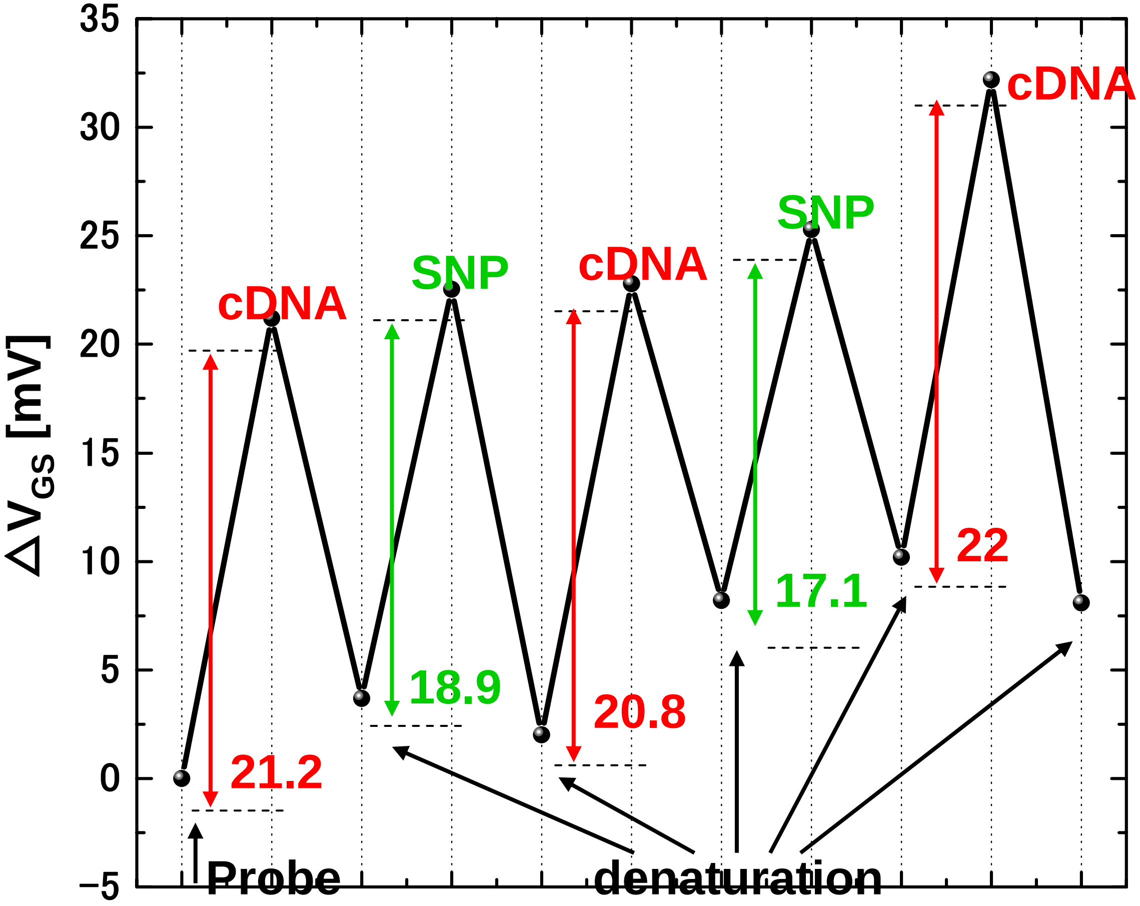


PBS (pH=7.4)
10 mM (NaCl)
Target DNA: 10 pM
21 bP

Song. Yang, Kawarada et al.,
Phys.Rev.E. 74, 041919 (2006).

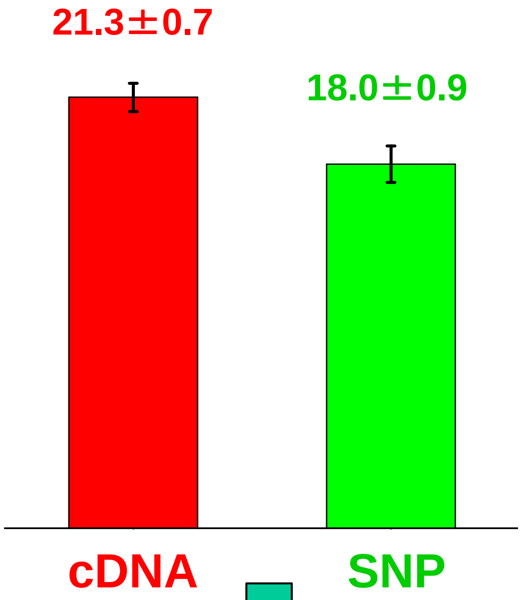
SNPs (1 bp mismatch) detection in static measurement

Repeat hybridization (cDNA or SNP) and denaturation



Song. Yang, Kawarada et al.,
Phys.Rev.E. 74, 041919 (2006).

ΔV_{GS} [mV]



SNP detection

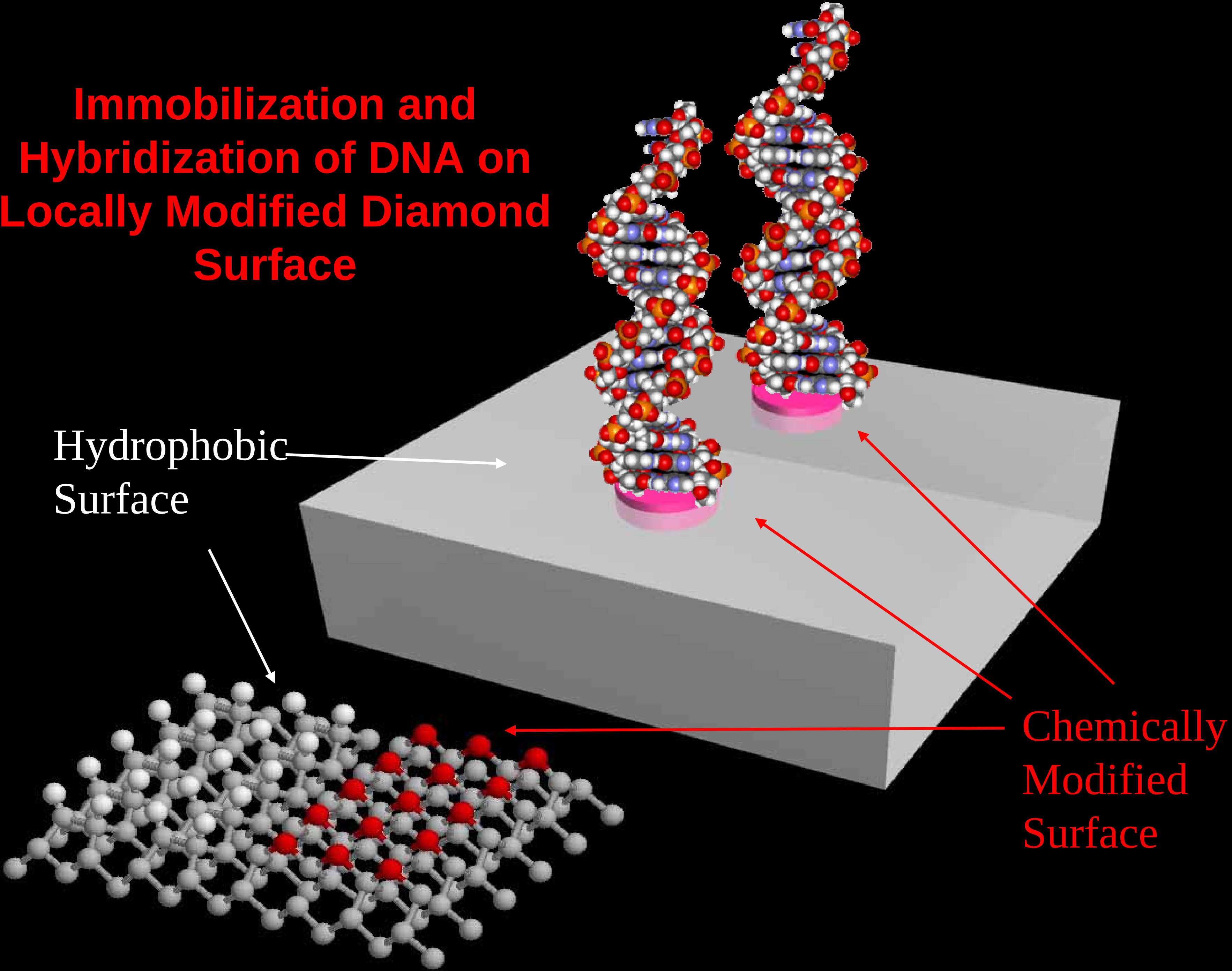
Hybridization temperature : RT
Buffer sol. : 1mM PBS DNA conc. : 100 [pM]
I_{DS} = -10 [μA] V_{DS} = -0.1 [V]

Summary II

Using directly immobilized probe DNAs on functionalized diamond, the detection of target DNAs has been investigated using two methods: fluorescence microscopy and SGFETs.

- Discrimination of single base (1bp) mismatched DNA by fluorescence microscopy by controlling surface termination.
- We realized DNA biosensor using solution gate (SG)FET to detect molecular charge.
- Large gate voltage shift of 20-30mV repeatable in the cycles of hybridization & denaturation indicating reusability.
- Distinction between cDNA, 1bp-mismatch and ncDNA sequences.
- In the future application, charge detection of RNA interaction with immobilized proteins

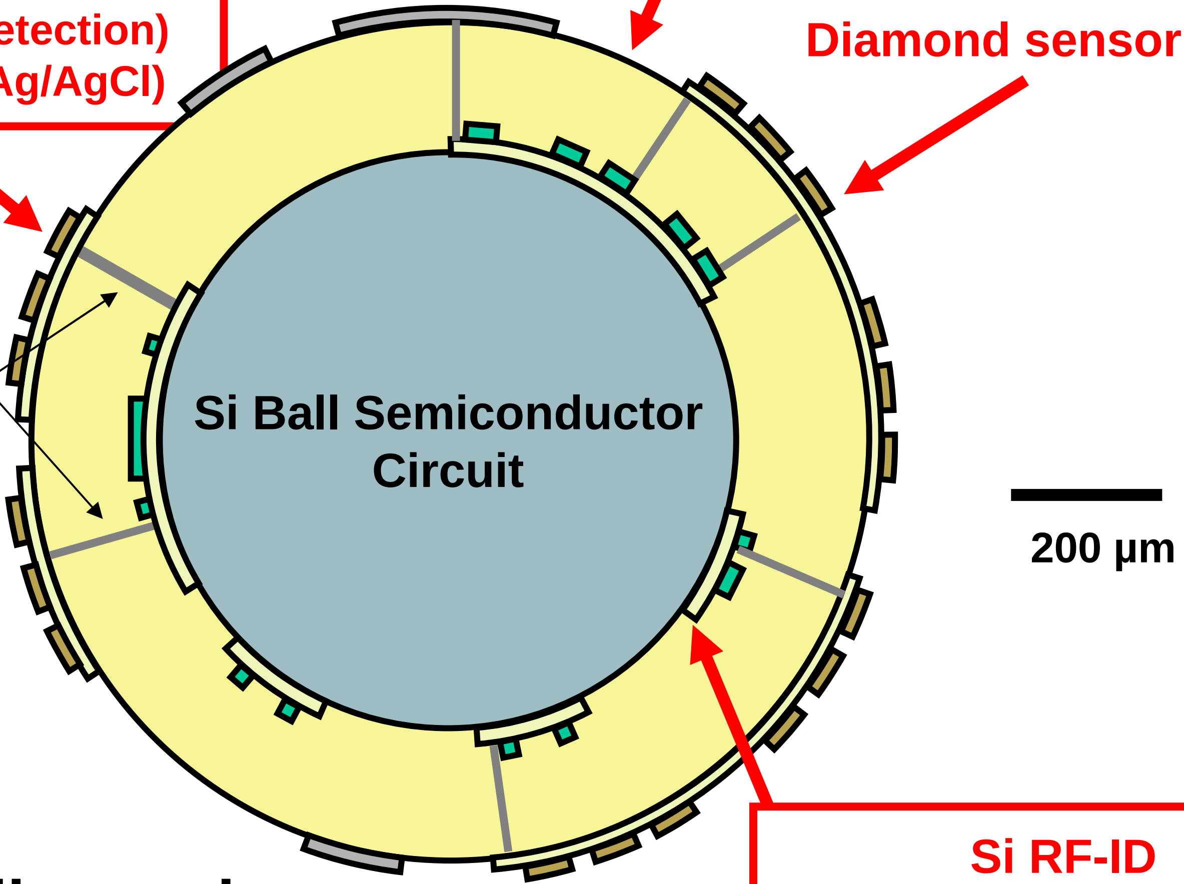
Immobilization and Hybridization of DNA on Locally Modified Diamond Surface



Hydrophobic Surface

Chemically Modified Surface

Biocompatible diamond sensors combined with ball semiconductor technology



Diamond sensor array

Integrated Bio Sensor
SGFET (potential detection)
Reference SGFET
SAW sensor (mass detection)
Standard electrode (Ag/AgCl)

Nano diamond coating

Diamond sensor array

Carbon nanotube interlayer connections

Si RF-ID

Signal processing (CMOS)
RF interface
Memory

Semiconductor is a stone where we sit

- “Sit on a stone for 3 years”

  石の上にも3年

  This old Japanese saying means that “with patience something can be realized”

- “Need to stay on one semiconductor for 30 years”

  1種の半導体に30年必要

  What we need here is not only patience,

  but “staying power” and “sustainable development”.