Diamond-Graphite-Diamond Heterostructures Produced by Implantation and HPHT Annealing for Lift-off Transfer and New Devices

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Tomsk 2017
Maximal breakdown voltage and mobility vs. doping

\[ E_{c,\, dia} = 10^7 \, V \cdot cm^{-1} \]

\[ V_B \approx \frac{\varepsilon_r E_c^2}{2qN_d} \]

\( E_c = \) electric breakdown field

\( N_d = 10^{17} \, cm^{-3} \)


diamond is 10 times better than all others

51, 14-21 (1999).
Band alignment and resistivity of diamond and graphite

Table:

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity ((\Omega\cdot\text{cm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>(10^{13} \div 10^{15})</td>
</tr>
<tr>
<td>Graphite</td>
<td>(10^{-5} \div 5 \cdot 10^{-3})</td>
</tr>
<tr>
<td>Laser-modified material</td>
<td>(3.6 \div 3.9)</td>
</tr>
<tr>
<td>Partially graphitized diamond ([1]): after ion bombardment after following annealing</td>
<td>(10^2) (\div) (10^{-3})</td>
</tr>
</tbody>
</table>


\[ J. \text{ Robertson}, \text{ phys. stat. sol. (a) 205, No. 9 (2008)} \]
Motivation

Normally-On MESFET: $I_{on} = 1300\text{mA/mm}$

Normally-Off MISFET & MESFET: $10\text{mA/mm}$

Normally-Off MOSFET: low current at $V_{GS} \leq 3 \text{ V}$!


Hirama K. et al. JJAP 51 (2012) 090112

H - transfer doped

Inversion channel MISFET

Partial C-O channel MESFET


$10\mu\text{A/mm}$ at 3.0 V
Diamond as a coolest material for Quantum Information Processing

Status of diamond relative to DiVincenzo criteria for Quantum Information Processing (QIP):

\[ T_D = 1860 \, K \]

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Low temp</th>
<th>Room temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Well-defined qubits</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>2. Initialization to a pure state</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>3. Universal set of quantum gates</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>4. Qubit-specific measurement</td>
<td>✓</td>
<td>Progressing well</td>
</tr>
<tr>
<td>5. Long coherence times</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>6. Interconvert stationary and flying qubits</td>
<td>Progressing well</td>
<td>Maybe</td>
</tr>
<tr>
<td>7. Transmit flying qubits to distant locations</td>
<td>Progressing well</td>
<td>Progressing well</td>
</tr>
</tbody>
</table>

`s: Better than excellent“ Nature Mat. 9, 468-469 (2010)

Write line


...but it is still not implemented!
1. Motivation for Diamond Electronics

2. Diamond–Graphite–Diamond by II & Lift-off Process

3. Diamond Junction & Field Effect Transistors (J- & FET’s)

4. Sensing by Membranes & NV Defects in Nanostructures

5. Conclusion
Forms and sizes of type Ib, IIb, IIa HPHT diamond samples

HPHT growth in Fe-Ni-C liquid from the seed

{111} Ib type crystal (left) and {100} (right) with the area up to 40 mm² was grown using (111) seed orientation for 3-4 carat size

Laser cleavage and grinding by diamond nanocrystal slurry

200-400 µm plates of {111} plates with the area up to 25 mm² were produced by laser pointing with subsequent cleavage along the plane of the spikes, grinding & polishing or CVD overgrowth.

Doped by B or N (1.0-100 ppm) and undoped (<0.1 ppb) samples were used.

How to produce 3-4 order of magnitude thinner slices ???

Using beam splitting: See our Poster no.26
Is injection implantation at $V > 50$ kV reasonable for multiple cut?

2:1 Relation in the flux between protons and molecular ions is needed. ESR source allows making this!
Defect profiles & graphitization after H+II + HPHT

Graphitization:

Hydrogen mol. 60 keV

\[ D_{crit} = 5 \times 10^{16} H^+ / cm^3 \]

Nitrogen 130 keV

\[ D_{crit} = 5 \times 10^{14} N^+ / cm^3 \]

**Graphitization**: \( N_{crit} = 10^{22} Vac / cm^3 \)

**Swelling**: \( T^{N_{gr}} > T^{N_{am}} > T^{N_{crit}} \) is due to 10-40% lower density in inner layer.
The pressure $p_0$ in blister (radius $R$, thickness of cup layer $h$) as a function of the maximum deflection $\delta$ is [*]:

$$p_0 = \frac{16 \tilde{E} h^3}{3 \langle R \rangle^4} \delta$$

[1]

$p_0$ is outer pressure. $\tilde{E} = E/(1-\nu^2)$ is biaxial elastic modulus with plane-strain modulus. $E = 175\pm5$ GPa Young’s modulus to [111] direction. Poisson ratio $\nu = 0.1$ [**]:

For VPHT with $h = 0.25 \ \mu$m, $R = 0.5 \ \mu$m,
$\delta = 0.03 \ \mu$m:  $p = 7.0$ GPa,

For HPHT with $h = 0.25 \ \mu$m, $R = 0.5 \ \mu$m,
$\delta = 0.006 \ \mu$m:  $p = 7.0$ GPa

Young's modulus to [0001] graphite is equal to $E = 32.5$ GPa and $\nu = 0.3$ :  $p = 1.6$ GPa,


TEM/HREM planar view: diamond & graphite layers after $\text{H}_2^+\text{II}$ & HPHT

Very rare defect region

Typical structure of glassy carbon layer

Dark field TEM of upper d-C layer (30÷50nm) with 12 diffraction spots due to nd-C twinning by $30^\circ$ rotation along $<111>$ direction leading to combination of cubic (d-C) and hexagonal (2H) diamond or grains

Glassy-C layer with thickness 100÷120 nm with vertical graphite nanolamellas inside with interplanar spacing $\Delta d = 0.35 \text{ nm}$

P.Nemeth et al. srep18381
First model for growth of graphite on (110) planes of diamond

After HPHT

Diamond (111)

GL-C:H \[\text{Diamond (111)}\]

After VPHT

Diamond (111)

GL-C:H \[\text{Diamond (111)}\]

Planar view

Bernal graphite on (121) microtwin

Diamond (111)

Diamond (111)

2:3 diamond growth model* – 3:2 graphite growth model for vertical planes

50 keV hydrogen molecule fluence $\Phi = 4 \times 10^{16} \text{ cm}^{-2}$ after HPHT annealing at $1200^\circ\text{C}$ 4 GPa 4 h

Graphite (nm): $0.335(111)$, $0.213(100)$,

Tetragonal distortion: $d_{111} = 0.354 \text{ nm}$, $d_{100} = 0.204 \text{ nm}$ with $72.7^\circ$ between $<111>$ and $<100>$ directions suggests mixed Bernal/rhombohedral graphene sheet package.
Second model for growth of graphite on (111) planes of diamond

1/1 graphite growth model corresponds to the experimental angle ~17° and shows increased distances between carbon atoms and graphene planes.

*V.P. Popov et al. AIP Conf. Proceed., 2012*
Hydrogen molecules ($H_2^+$), 50 keV, $(1\div13)\times10^{17}$ cm$^{-2}$
+ Nitrogen (N$^+$), 120 keV, $3.5\times10^{16}$ cm$^{-2}$ (through Al-mask for contacts)
HPHT treat.: $P=4\div8$ GPa
$T=1200\div1600^\circ$C, 4 h (BARS)
VPHT: $P=10^{-3}$ Pa

J-K Lee, Scie. Rep. DOI: 10.1038/srep39624

Theoretic bigraphane interplanar distance* $\sim0.45\div0.50$ nm

Nanographane? or twisted AA'?
Applications for DGD-heterostructures

Amplifying of NV-centers PL in d-C Ib by E-field

CN-heterojunctions

Graphite H-C Diamond

Graphite H-C Diamond

CN

Sample B10

N⁺, 50 keV, 4*10¹⁷ cm⁻²

Test structures for conductivity

Hydrogen molecules ($H_2^+$), 50 keV, $(1\div13)\times10^{16}$ cm$^{-2}$

+ Nitrogen ($N^+$), 130 keV, $3.5\times10^{16}$ cm$^{-2}$ (through Al-mask for contacts)

VPHT treat.: $P=10^{-3}$ Pa
HPHT treat.: $P=4\div8$ GPa
$T=1200\div1600^\circ$C, 4 h

FIB litography +

standard lithography with Al masks

Nitrogen implantation for contact pads

Al etching +

thermal annealing
Quantum correction* due to e-e interaction in diffusion channel:

\[
\sigma(T) = \sigma(0) + \Delta \sigma_{e-e}(T) = \sigma(0) + \beta \cdot T^{1/3}
\]

If \( \sigma(0) < 0 \) for degenerate semiconductors in cryogenic \( T \)-range, then the conductivity has nonmetallic character, i.e. below MIT, but if \( \sigma(0) > 0 \) then the conductivity is quasimetallic after 1200°C or above MIT.

Variable range hopping mechanism of conductivity

\[
S(T) = S_0 \cdot T^{-1/2} \cdot \exp \left[ -(T_0/T)^{1/4} \right]
\]

\( T_0 = 16/a^3 k N(E_F) \)

\( a \) - radius of hopping site

sp2 bond - \( a = 1.2 \) nm

When conductivity becomes metallic? Reznik et al. This happens when density of states \( N(E_F) \) reaches the value \( N_0(E_F) \) determined by the relation \( N_0(E_F) \cdot a^3 = 1 \), i.e. \( N_0(E_F) = 1/a^3 = 6 \times 10^{20} \) states/(eV*cm³) for \( a = 1.2 \) nm.

Semimetallic mechanism of conductivity
240 & 32 nm membrane from diamond-graphite-diamond (DGD) heterostructures produced by N\textsuperscript{+} & H\textsubscript{2}\textsuperscript{+} II

Absorption bands at UV 100 and 300 nm indicate a presence of graphite inclusions after 1600°C.

*V.P. Popov et al. AIP Conf. Proceed., 2012
240 nm membranes from diamond-graphite-diamond heterostructures produced by \((N^+ + H_2^+)\)II + HPHT + Anodic Etching

No other PL lines at laser excitation at \(\lambda_{ex} \leq 514.5\) nm after 1600°C, only small \(G^*\)-line and four times larger FWHM for UV RS due to residual stresses*


Bonding of diamond 30 nm film to PMMA or glass substrate

Hydrogen molecule fluence $\Phi = 8 \times 10^{16}$ cm$^{-2}$ after HPHT annealing at 1200°C 1h

HII: H$_2^+$ 50 keV, $8 \times 10^{16}$ cm$^{-2}$, HPHT, 1200°C, 5GPa 2h,

AO of 110 nm Gl-C and transfer of 290 nm diamond on PMMA substrate (delamination by residual stress in diamond membrane)
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Diamond vs. Silicon p-n Junctions

Measured I-V characteristics of p-n mesa junctions at RT after 1200°C 4 GPa

I-V characteristics of equally doped p-n junctions at RT simulated by TCAD Synopsys
Design of Diamond Hetero or Schottki Barrier n-MISFET

Diamond body. The drain and source are made from Al,Pt Schottki or n⁺-type (10^{19} \text{cm}^{-2}) silicon carbide Hetero Barrier and located at the edges of the diamond body (in one plane):

• Full length of the transistor is 200 nm.
• The length of the gate is 100 nm.
• The length of the channel is 104 nm.
• The length of drain & source is 20 nm.
• The thickness of diamond layer is 20 nm.
• The thickness of the gate oxide is 2 nm.
• Top aluminum (Al) gate.
• The back oxide thickness is 20 nm on Al plate.
Electron Density in Diamond FETs with Schottki Barriers

I-V characteristics of SB MISFET at RT simulated by TCAD Synopsys

No large difference in SB MISFET for four different parameter sets by TCAD Synopsys

Ion = 10mA/mm: $E_{\chi}< -6.9$ eV SB p-MISFET $E_{\chi}> -1.8$ eV for SB p-MISFET at $V_g>+2$ V
E-Bands & Current Density in Diamond Hetero n-MISFET

Bottom of conduction band and Electron Density at +1 nm under the surface
**HeterobARRIER n-MISFET vs. inversion channel p-MOSFET**

\[ I_{ds} = 1 - 100 \text{ mA/mm at 500°C} \]

in dependence on the \( m_t \) under the barrier

HeterobARRIER n-MISFET vs. inversion channel p-MOSFET

Vg = 6V: 5 µA/mm

I_{ds} = 100 mA/mm at 500°C

But we need to account correctly the dependence $\mu = \mu(E)$

Heterobarrier p-JFET with n-type g-C3N4 mesh

CN-heterojunctions with $I_{off}/I_{on} \sim 10^{-3}$

*Iwasaki T. et al. JEDS 5 (2016) 2624301
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Diamond & Multigraphene Membranes as Silicon FET gate

I-V characteristics of membrane gated FET with three gate lengths simulated by TCAD Synopsys

Stark Effect at NV-centers in forward biased p-i-n diode

Exciton luminescence ($V_{FB}=35\, \text{V}$)

$E_{\text{dia}} = 10^6 \, \text{V} \cdot \text{cm}^{-1}$

Splitting in Stark shift for 2 NV$^-$ groups

$E_{p-n} = 10^3 \, \text{V} \cdot \text{cm}^{-1}$

$E_{NV0/-} = E_C - 2.58 \, \text{eV}$

$\delta_{1,2} \approx 600, 400 \, \text{GHz}$

$E_{p-n} = 10^6 \, \text{V} \cdot \text{cm}^{-1}$

The splitting allows to control of the spins in differently oriented NV$^-$ groups along <111> axes

ODMR of NV’s in 300 nm N⁺ implanted layer at high temperature

\[ H = D \left[ S_Z^2 - S(S+1)/3 \right] + \gamma [B + b(t)] \cdot S + E(S_x^2 - S_y^2), \]

45% of the NV’s are \( \perp \) to the surface\(^{***}\)

If transverse spin-relaxation time \( T_2^* \) is:

\[ T_2^* = 1/(\pi \delta) = 52 \text{ ns} \]

Spin-relaxation time \( T \) due to dipolar coupling is:

\[ T_{NV} \approx 1/[(g_s \mu_B)^2 n_{NV}] = 700 \text{ ns} \]

\[ T_{NV} \approx 1/[(g_s \mu_B)^2 n_{Ns}] = 200 \text{ ns} \]

\( T \) is limited by high \( n_{Ns} \)

Highest \( T_{NV} \approx 500 \text{ ms for } n_{Ns} = 10^{15} \text{ cm}^{-3} \)

\[ T_{NV} \approx 1/[(g_s \mu_B)^2 n_{NV}] = 1 \text{ s} \]

\[ T_{NV} \approx 1/[(g_s \mu_B)^2 n_{Ns}] = 130 \text{ ms} \]

\( \Delta = 62 \text{ MHz} \quad \Delta = 60 \text{ MHz} \quad \Delta = 152 \text{ MHz} \)

\( D = 2870 \text{ MHz} \)

\( \delta = 6.3 \text{ MHz} \)

\( \Delta = 151 \text{ MHz} \)

ODMR of NV’s in 300 nm N⁺ implanted layer at high temperature

\[ H = D \left[ S_Z^2 - S(S+1)/3 \right] + \gamma [B + b(t)] \cdot S + E(S_x^2 - S_y^2), \]

No hyperfine splitting* for NII:

\( (3.1 \text{ MHz})/(9.5 \text{ MHz}) \rightarrow \delta = 6.3 \text{ MHz} \)


Magnetic dipole coupled spin arrays

\[ E_{\text{md}} \sim \frac{1}{d^3} \rightarrow d \sim \frac{3}{T_2} \]

**T_2 limit**

Error in collectively enhanced quantum gates

\[ \varepsilon = 1 - \exp\left[-\left(\frac{4t_\pi}{T_2^*}\right)^3\right] \]

For \( \varepsilon = 10^{-4} \rightarrow T_2^* = 11 \text{ ms} \)
The probability to find analogical or other charged centers with content \([C_{Ns}] = 2.5 \times 10^{13} \text{ cm}^{-3}\) in neighborhood of 10 nm layer on the distance \(r\) and determines as \(\exp(-\pi[C_{Ns}]R^2) = 1/2\). Then the distance \(R\) is equal to \(R \approx 0.47([C])^{-1/2} = 1 \times 10^{-6} \text{ cm} = 10 \text{ nm}\).

**Visible PL at 575 and 637 nm of NV\(^0\) & NV\(^-\) with content \([C_{NV}] = 5 \times 10^{13} \text{ cm}^{-3}\) at LNT**

FWHM of NV\(^-\) is \(\delta = 170 \text{ GHz}\) or \(230\pm 10 \text{ pm}\) instead of \(\delta = 30 \text{ GHz}\) for single NV\(^-\). NV’s mainly in clusters!

FWHM for 0.2–20ppm NV’s is the same for bulk, HNI & HII diamond

*V.P. Popov, et al*. ICW-2010, Kyoto 2010
PL CLM of NV ensembles in Ar$_{27}$ Cluster Ion Implanted Diamond

The probability to find analogical or other charged centers with content $[C] = 2.5 \times 10^{13}$ cm$^{-2}$ in neighborhood on the distance $r$ and determines as $\exp(-\pi [C] R^2) = 1/2$.

Then the distance $R$ is equal to $R \approx 0.47([C])^{-1/2} = 1 \times 10^{-6}$ cm = 10 nm (anneal. 850$^\circ$C)

$$425\mu m$$

**Number of NV centers $N_{NV}$ in spice**

- $N_{NV} = 1$ - 25
- $N_{NV} = 2$ - 50
- $N_{NV} = 3$ - 100
- $N_{NV} = 4$ - 150
- $N_{NV} = 5$ - 200
- $N_{NV} = 10$ ...

**NV$^-$ ensemble spots with area content $[C_{NV}]_s = 3 \times 10^6$ cm$^{-2}$ or $1/300$ of $[N_{Cl}]$!**

Average distance $R$ is equal to $R \approx 0.47([C_{NV}])^{-1/2} = 1.6 \times 10^{-4}$ cm = 1.6 $\mu$m at RT

V.P. Popov, et al. ICW-2010, Kyoto 2010
Solid State Lenses with One NV Ensemble made by Ga⁺ FIB

532 nm green laser beam with 300 nm in diameter

PL increasing for solid state lenses due to a suppression of inner reflection

Intensity, arb. un.

Wavelength, nm

But what is the influence of FIB induced defects?

\([C_{NV}]_s = 3 \times 10^6 \text{ cm}^{-2}\) than average content in lens is \(<N_{NV}> = 50 \text{ pcs.}\)

5x increase in NV⁻ PL intensity, but we need a regular matrix!
ODMR of NV’s (~50 pcs) in H⁺II & annealed pillars of 300 nm in the height

For H⁺II only strain splitting is observed:

\[(3.1 \text{ MHz})/(6.3 \text{ MHz}) \rightarrow \delta = 3.2 \text{ MHz}\]

If transverse spin relaxation time $T_2^*$ is:

$T_2^* = 1/(\pi \delta) = 100 \text{ ns}$

Spin-relaxation time $T$ due to dipolar coupling:

$T_{NV} \approx 1/[(g_s \mu_B)^2 n_{NV}] = 3.5 \mu s$

$T_{NV} \approx 1/[(g_s \mu_B)^2 n_{Ns}] = 140 \text{ ns}$

$T$ is limited by high $n_{Ns}$!

$E= 6.3 \text{ MHz}$ corresponds to the strain

$\varepsilon = +1.5\%$

$\langle \text{NV's} \rangle \sim 50 \text{ pcs}$
Stimulated spin echo for $T_2$ measurements by MW pulse ODMR at constant laser excitation beam.

\[
\frac{I_3}{I_4} = 1.3 = \exp \left( -\frac{2}{\tau} + \frac{5}{\tau} \right)
\]

\[\Rightarrow \quad 30\% \text{ decrease in ODMR dip after } 5 \mu s\]

\[\text{means} \quad T_2 \text{ value } \sim 12 \mu s\]
1. Hydrogen implantation with fluences $\Phi > 10^{17} \text{ cm}^{-2}$ and HPHT annealing provide the buried conductive layer of mixed graphite forms with the resistivity $< 10^{-3} \text{ Ohm} \cdot \text{cm}$ inside the diamond.

2. Lift-off technique allows forming free and transferred membranes of diamonds as thin as 30 nm that are prospective for thin film vertical JFETs with a saturation current $I_{on} = 50 \text{ mA/mm}$.

3. The results for Schottki Barrier MISFET simulation using SB source-drain contacts show $I_{on}$ as high as 100 mA/mm for optimized SB metals, or ~10 times higher than in normally-off MESFETs with H-transfer doping.

4. Hetero Barrier n-MISFET simulation with CN S-D regions shows the $I_{on}$ as high as 100 mA/mm for optimized S-D doping or about ~100 times higher than in inversion channel n-MOSFETs but $I_{on}$ depends strongly on effective mass of carriers under the barrier.
Conclusion

1. Suspended diamond membranes as a gate of silicon FETs service as a highly sensitive sensors of displacements in the nanoscale range

2. NV-centers at the concentration 0.2-20 ppm in 30-300 nm layers and membranes have practically the same spectral characteristics as in the bulk diamond crystals

3. Charge state and ZPL position of NV-centers are effectively controlled by inner electric fields in p-n junction

4. NV center relaxation and spin coherence times are determined mainly by the interaction with nearest nitrogen donors and should be increased for QIP

5. NV matrices are the promising candidate for magnetic, electric, and spin nanoscopy and NMR spectroscopy with nanoscale resolution
Our thanks
to the colleagues from the Institutes of Semiconductor Physics, Geology and Mineralogy of SB RAS and Melbourne University:

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Dr. A.A. Kalinin for HPHT treatment,
Dr. S. Rubanov for SEM analysis.

Thank Your for Attention!