RECENT PROGRESS IN THE FIELD OF DIAMOND HETEROEPITAXY ON IRIDIUM

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OUTLINE

- Motivation
- Heteroepitaxy of diamond: a brief review
- Bias enhanced nucleation (BEN)
- Diamond films on Iridium: state of the art
- Scaling-up: state of the art
- Understanding BEN on Iridium: A model summarizing the major observations
MOTIVATION

Heat spreaders

Source: E6

Windows for high power CO₂-lasers

Source: FHG-IAF Freiburg

Coatings on tools for drilling and milling (wear reduction)

Is there any need for single crystals?
WHAT'S THE NEED FOR SINGLE CRYSTALS? (LIMITING PROPERTIES OF POLYCRYSTALLINE FILMS)

Mechanical properties

Strength:

Theoretical values: 120-190 GPa

Diamond single crystals (exp.): 2.8 GPa


Electrical properties

Charge carrier mobilities (holes):

Single crystals: 3800 cm²/Vs

Polycrystalline films: 30-40 cm²/Vs

Heteroepitaxial layers on Si(001):

165 cm²/Vs (bei RT)


Diamond detectors

HOMOEPITAXY

WIRED (Sept. 2003)
Linares (Apollo).... the company is producing 10-millimeter wafers but predicts it will reach an inch square by year's end and 4 inches in five years.
HETEROEPITAXY OF DIAMOND: SEARCHING FOR THE IDEAL SUBSTRATE MATERIAL

(a) c-BN(001)
(b) c-BN(111)
(c) Al₂O₃(0001)
(d) Ni(001)
(e) Ni(111)
(f) Pt(111)
(g) Si(001)
(h) β-SiC(001)
(i) Ir/MgO(001)
## HETEROEPITAXY OF DIAMOND: SEARCHING FOR THE IDEAL SUBSTRATE MATERIAL

<table>
<thead>
<tr>
<th>Substrate</th>
<th>First Publication</th>
<th>Current state of the art</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond on $\beta$-SiC:</td>
<td>Stoner &amp; Glass 1992</td>
<td>Tilt: 0.6° Twist: ~2.5°</td>
</tr>
<tr>
<td>Diamond on silicon:</td>
<td>Jiang &amp; Klages 1992</td>
<td>Tilt: ~1° Twist: ~4°</td>
</tr>
<tr>
<td>Diamond on Pt:</td>
<td>Tachibana, Kobashi, Shintani 1996</td>
<td>Tilt: 1.1° Twist: -</td>
</tr>
<tr>
<td>Diamond on Ir:</td>
<td>Ohtsuka, Suzuki, Sawabe, Inuzuka 1996</td>
<td>Tilt: 0.16° Twist: 0.34°</td>
</tr>
</tbody>
</table>

Further materials: c-BN, Cu, Ni, Co, Re, TiC, Ni$_3$Si, Ni$_3$Ge, Al$_2$O$_3$
BIAS ENHANCED NUCLEATION (BEN)

Microwave plasma ball

Substrate
BIAS ENHANCED NUCLEATION (BEN)

Bombardment of the surface with pos. ions (U typically: 100 - 300V)

Nucleation densities up to $10^{11}$ cm$^{-2}$
(on Si, only partially oriented)

Epitaxy on different materials:
- covalent bonding (Si) → metals (Ir)

Modification: pure DC discharge
COMPARISON:
DIAMOND ON Si ⇔ DIAMOND ON Ir/SrTiO$_3$

The film surface

Diamond on silicon

The cross section

Diamond on Ir/SrTiO$_3$(001)
INTERNAL DEFECT STRUCTURE:
TRANSMISSION ELECTRON MICROSCOPY (TEM)

During textured growth:
- closed network of grain boundaries
- isolated short defect bands (quasi single crystal)

Schematic sketch of defect bands from TEM image in (c)
The technological challenge: finding an appropriate multilayer system
OXIDE SINGLE CRYSTALS vs. BUFFER LAYERS ON SILICON

Requirements:

a) Growth of single crystal iridium films

b) Thermally compatible with diamond

Dia/Ir/YSZ/Si(001)

Dia/Ir/SrTiO$_3$/Si(001)
IRIDIUM ON SILICON VIA SrTiO$_3$ BUFFER LAYERS

Epitaxial iridium directly on silicon not possible
→ Oxide buffer layers between silicon and iridium

SrTiO$_3$ buffer layer by MBE growth (mosaicity: tilt/twist: 0.43°/1.36°)

Mosaicity (angular spread) of the iridium much lower than that of the underlying oxide buffer layer

2. THE ALTERNATIVE CONCEPT: YSZ ON Si PREPARED BY PLD

Pulsed laser deposition (PLD) setup

Laser pulse

KrF excimer laser
25 ns pulses of 850 mJ

Yttria stabilized zirconia (YSZ) film deposition:
- no removal of the silicon oxide
- ablation target: (ZrO$_2$) stabilized with Y$_2$O$_3$
- $5 \times 10^{-2}$ Pa oxygen (First 600 pulses without oxygen)
- substrate temperature: 825°C
- thickness: 20 nm (40 nm)
HETEROEPITAXIAL IRIDIUM ON YSZ/Si(001)

Rocking curve

Azimuthal scan

Order of magnitude lower mosaic spread for the iridium film than for the YSZ
MICROSTRUCTURE AND INTERFACE

Dislocation density of iridium: $\sim 10^{11}$ cm$^{-2}$

Crystalline interface Ir/YSZ

Dislocation density of YSZ: $\sim 10^{12}$ cm$^{-2}$

Crystalline quality of the iridium is significantly higher than that of the YSZ directly from the interface

$\Rightarrow$ Mechanism?
MECHANISM OF TEXTURE IMPROVEMENT DURING IRIDIUM DEPOSITION

Iridium islands on misoriented oxide

Mechanism I: averaging process during the coalescence of the iridium islands

Mechanism II: burying of defects
THICK DIAMOND FILMS ON Ir/YSZ/Si(001)

45 µm thick diamond film with good adhesion to the substrate
WHAT IS THE BEST STOICHIOMETRY FOR YSZ BUFFER LAYERS?

2 (of 3) different ablation targets

Laser plume
During ablation

Tetragonal => cubic YSZ

SEM images of Ir surfaces
SCALING-UP TO 4\"": YSZ

YSZ:
grown by PLD on 4-inch silicon (001) wafers

Homogeneous thickness (10% variation) measured by ellipsometry
IRIDIUM WAFERS

Preparation of the iridium layer by e-beam evaporation on 4-inch YSZ/Si(001) wafers

Mirror-like surface, thickness between 135-150nm (RBS)

AFM: low RMS (~1nm), large terraces
RHEED along [110]: streaky pattern
→ High crystalline quality of the surface

XRD

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GROWTH OF DIAMOND ON 4" Ir/YSZ/Si(001) WAFERS

SEM

Thickness: 40 µm

XRD

Rocking curve: (004) Diamond

FWHM = 0.16°

Azimuthal scan: (311) Diamond

FWHM = 0.34°

lowest values reported up to now
IR(111): EXTREMELY LOW TWINNING RATIO

Ir(111)/Al₂O₃(0001)

Ir(111)/YSZ(111)/Si(111)

Twinning < 10⁻⁴

Only one texture component

⇒ Monocrystalline metal films possible
Why is Ir so much better than any other substrate?

=> Understanding BEN on Ir
SPECIAL FEATURES OF DIAMOND ON IRIDIUM

Highest density of oriented grains

Cross section TEM image after 2 min growth

Dia/Si(001)

Dia/Ir/SrTiO₃(001)

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NUCLEATION ON SILICON vs. IRIDIUM

(a) CURRENT (mA) vs. BIASING TIME (min)

(b) NUCLEATION DENSITY (cm⁻²) vs. BIASING TIME (min)

(c) Micrograph with biasing time of -200 V

(d) CURRENT (A) vs. BIASING TIME (min)

BEN on Ir/SrTiO₃(001)
U_{Bias} = -250 V
Diamond nucleation occurs under conditions under which diamond grains are etched!!!
CLASSICAL NUCLEATION THEORY

Nucleation under etching conditions contradicts classical nucleation theory
THE IRIDIUM SURFACE AFTER BEN

Bright domains in the SEM

Correspondence
Domains \leftrightarrow Diamond islands??

Growth step 1 year later

(a)
What is the amount of carbon at the Ir surface after BEN?
CROSS SECTION TEM IMAGES OF BEN SAMPLE 1 & 2

- A slit is clearly visible
- On the flat sample: continuous with rather homogeneous thickness
- Thickness: ~ 1 nm
The internal structure of the BEN layer?
HIGH RESOLUTION IMAGES OF THE INTERFACE REGION (FLAT & ROUGH SAMPLE)

- Epitaxial iridium covering layer (preferentially on rough sample)
- Amorphous regions?!
- Atomically resolved structures show only iridium’s lattice constant

In addition: No diamond related spots in LEED or RHEED
X-RAY PHOTOELECTRON DIFFRACTION (XPD)

- no XPD C1s pattern in case of unsuccessful nucleation
- XPD C1s pattern similar to highly oriented polycrystalline diamond in case of successful BEN
- anisotropy values ➔ compatible with diamond grains of 10 nm lateral size !??
The topographic signature of the domains?
TOPOGRAPHIC SIGNATURE OF THE DOMAINS

Nucleation in a pure DC discharge

MEAN STEP HEIGHT: 1.1 ± 0.1 nm
A MODEL DESCRIBING THE STRUCTURE OF
THE BEN LAYER INCLUDING THE DOMAIN

- The layer formed during BEN consists of **3 different carbon phases**
- Significantly lower density of the amorphous precursor phase
The temporal dynamics of pattern formation?
How did they start to grow?

LATERAL GROWTH AND NUCLEATION

EROSION AND DISSOLUTION

→ domain formation (or dissolution) is a continuous process
SUMMARY

- **Heteroepitaxial diamond growth**: a promising concept for the realization of large area single crystal diamond layers
- **Bias enhanced nucleation**: a powerful nucleation method
- **Iridium**, a unique material for the nucleation of diamond
- **SrTiO₃ and YSZ**: two alternative buffer layers to grow diamond/diamond/Ir films on silicon
- New experiments on the **pattern formation** (“domains”) during BEN on Ir
- A **model** was presented which can consistently explain a large variety of experimental observations

Thanks for your attention!
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