NoRHDia Workshop 2008 09 -10 June 2008

RECENT PROGRESS IN THE FIELD OF DIAMOND HETEROEPITAXY ON IRIDIUM

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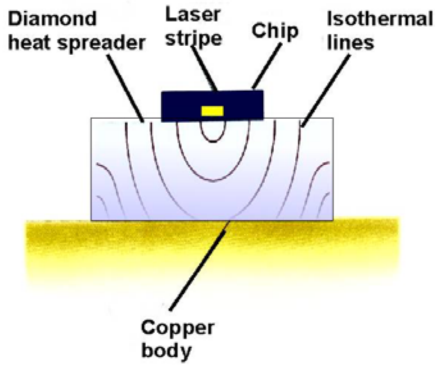
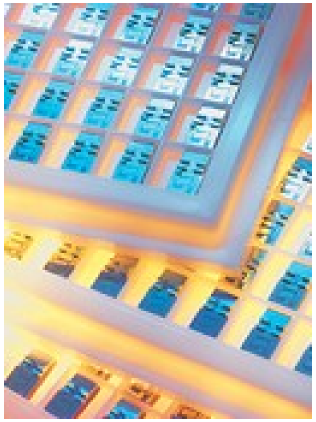
OUTLINE

- **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

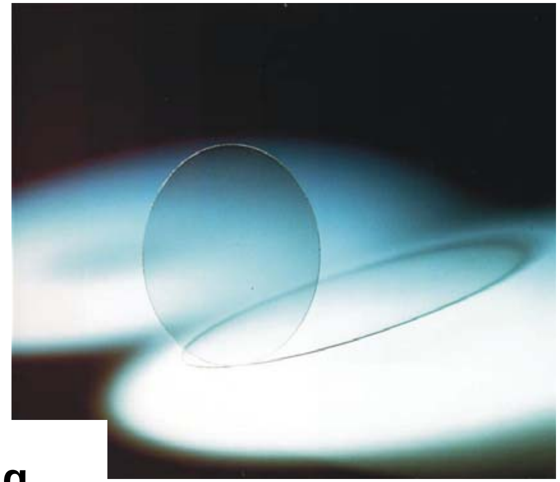
Heat spreaders





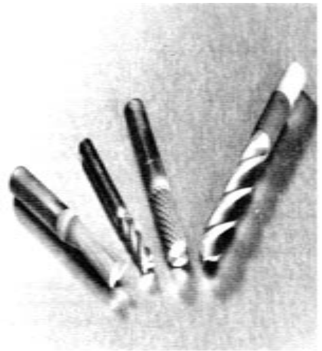
Source: E6

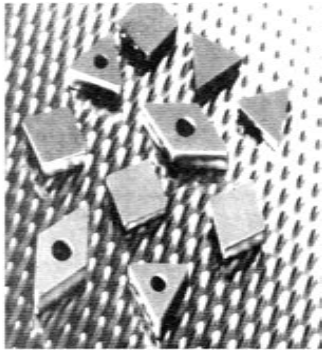
Windows for high power CO_2-lasers



Source: FHG-IAF Freiburg

Coatings on tools for drilling and milling (wear reduction)





Is there any need for single crystals?

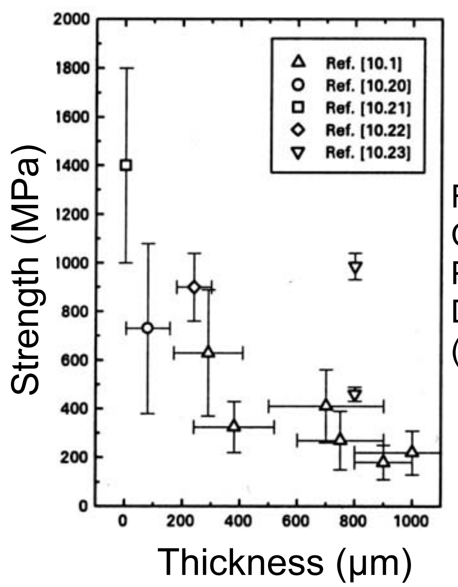
WHAT'S THE NEED FOR SINGLE CRYSTALS?
(LIMITING PROPERTIES OF POLYCRYSTALLINE FILMS)

Mechanical properties

Strength:

Theoretical values: 120-190 GPa

Diamond single crystals (exp.): 2.8



From: B. Dis
C. Wild: Low
Pressure Sy
Diamond Sp
(1998)

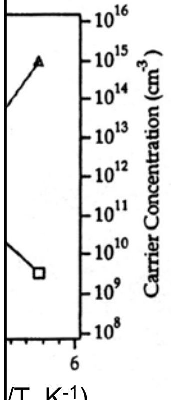
Electrical properties

Charge carrier mobilities (holes):

Single crystals: 3800 cm²/Vs

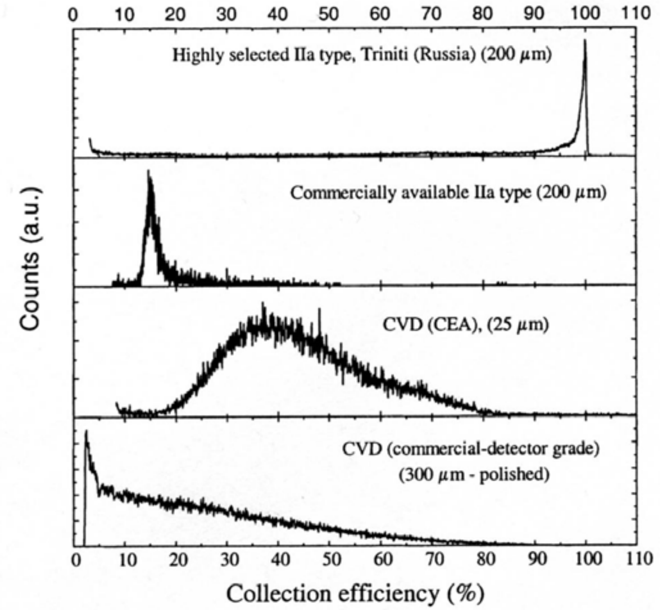
-40 cm²/Vs

on Si(001):



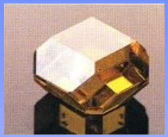
62 (1993) 2347

Diamond detectors



Bergonzo et al., Diamond Relat. Materials 10 (2001) 631.

HOMOEPITAXY



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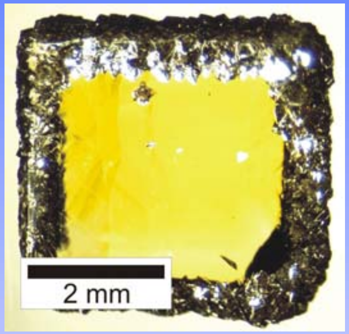
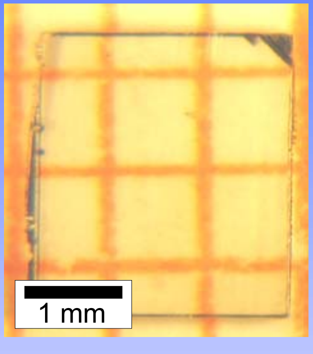
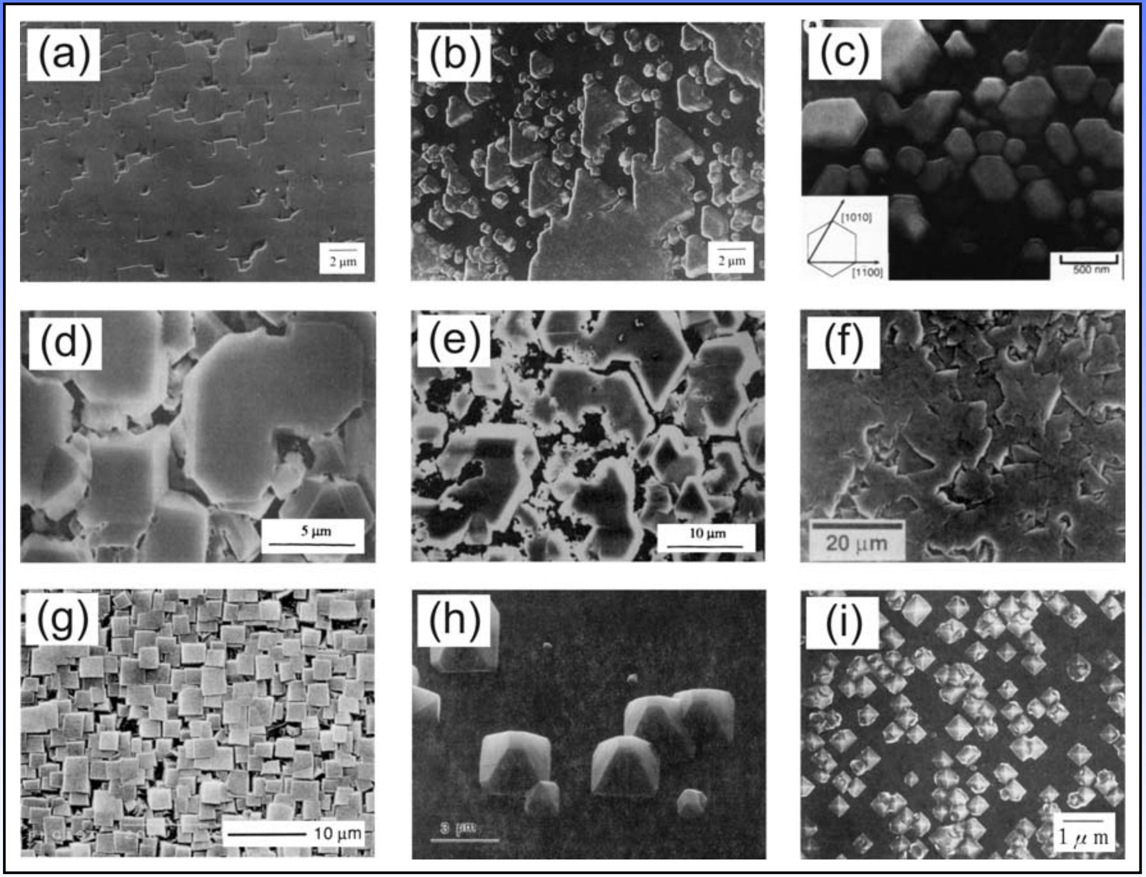




WIRED (Sept. 2003)
Linares (Apollo).... *the company is producing 10-millimeter wafers but predicts it will reach an inch square by year's end and 4 inches in five years.*

HETEROEPITAXY OF DIAMOND: SEARCHING FOR THE IDEAL SUBSTRATE MATERIAL



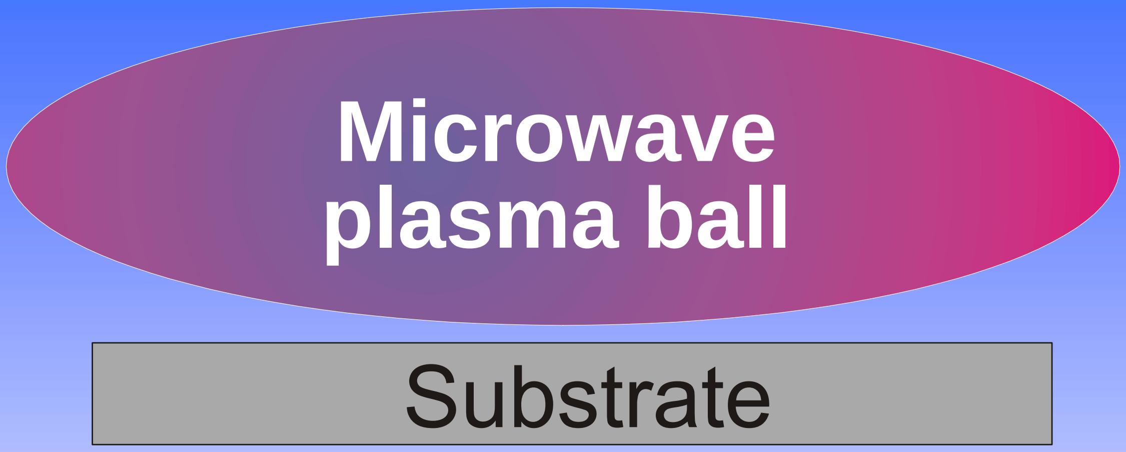
(a) c-BN(001)
(b) c-BN(111)
(c) Al_2O_3(0001)
(d) Ni(001)
(e) Ni(111)
(f) Pt(111)
(g) Si(001)
(h) β-SiC(001)
(i) Ir/MgO(001)

HETEROEPITAXY OF DIAMOND: SEARCHING FOR THE IDEAL SUBSTRATE MATERIAL

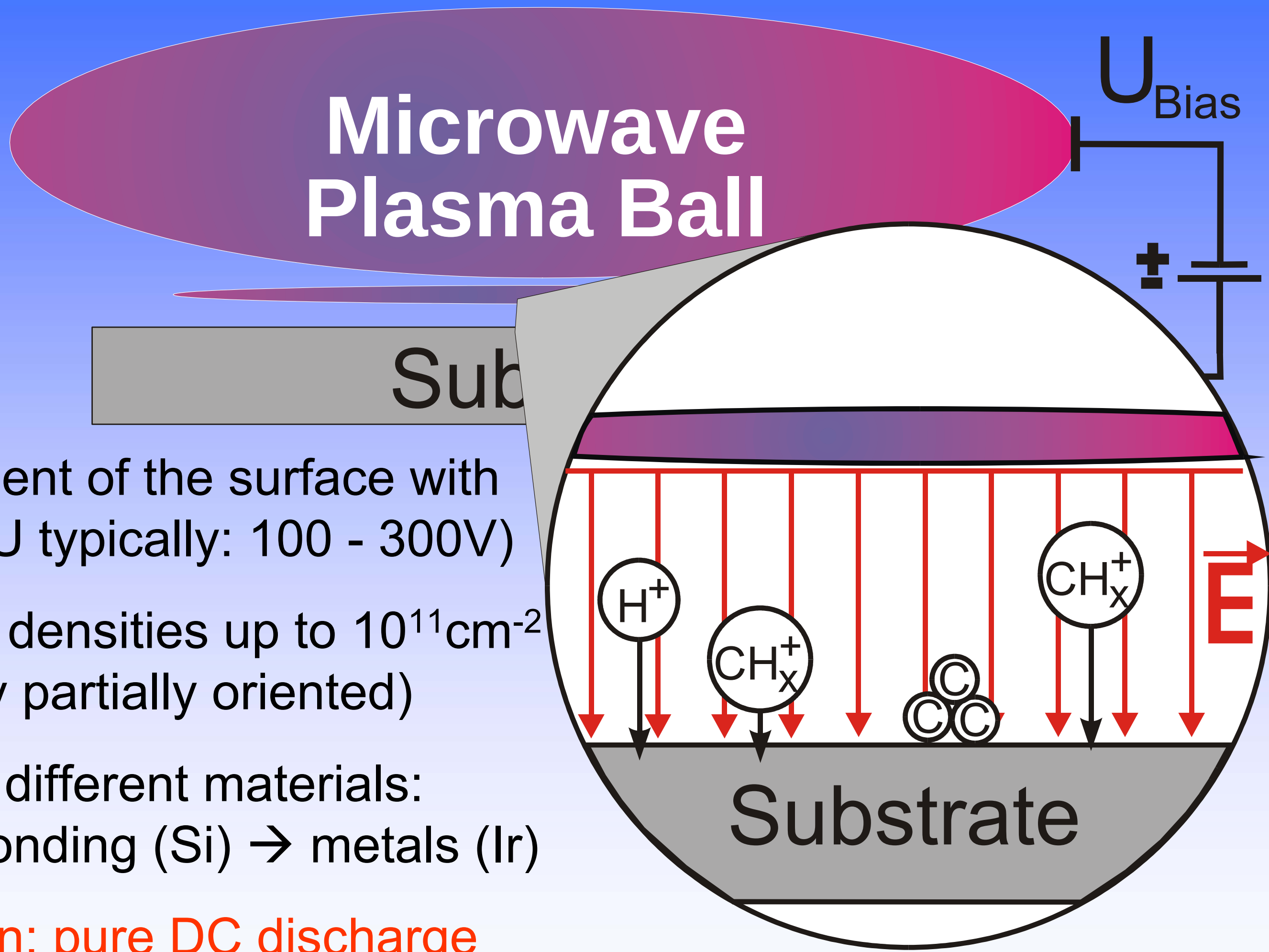
Substrate	First Publication	Current state of the art
Diamond on β-SiC:	Stoner & Glass 1992	Tilt: 0.6° Twist: ~2.5°
Diamond on silicon:	Jiang & Klages 1992	Tilt: ~ 1° Twist: ~4°
Diamond on Pt:	Tachibana, Kobashi, Shintani 1996	Tilt: 1.1° Twist: -
Diamond on Ir:	Ohtsuka, Suzuki, Sawabe, Inuzuka 1996	Tilt: 0.16° Twist: 0.34°

Further materials: c-BN, Cu, Ni, Co, Re, TiC, Ni_3Si, Ni_3Ge, Al_2O_3

BIAS ENHANCED NUCLEATION (BEN)



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)

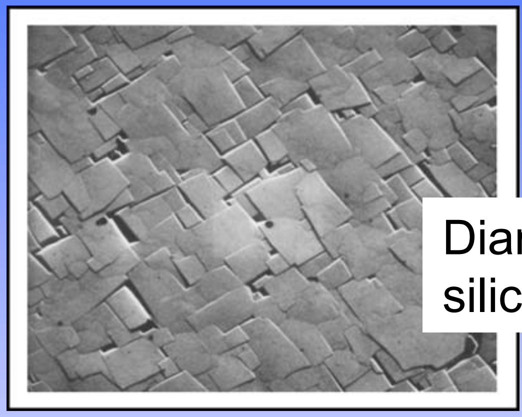
Epitaxy on different materials: covalent bonding (Si) → metals (Ir)

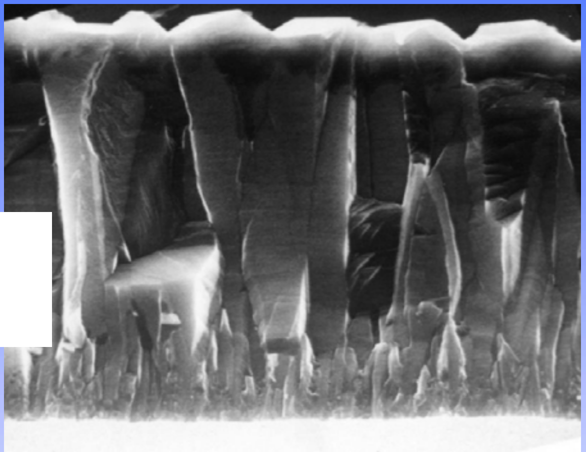
Modification: pure DC discharge

COMPARISON:
DIAMOND ON Si⇔DIAMOND ON Ir/$SrTiO_3$

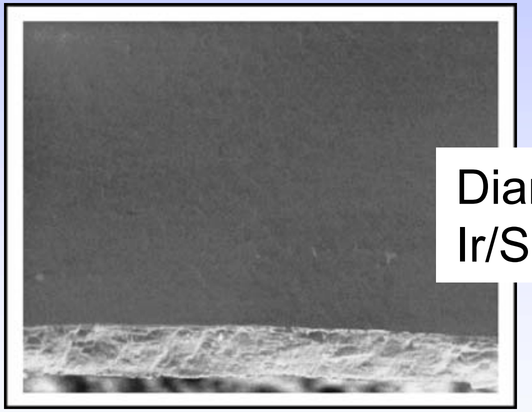
The film surface

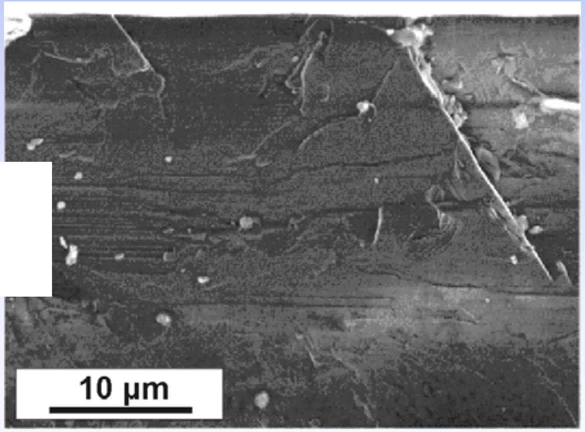
The cross section





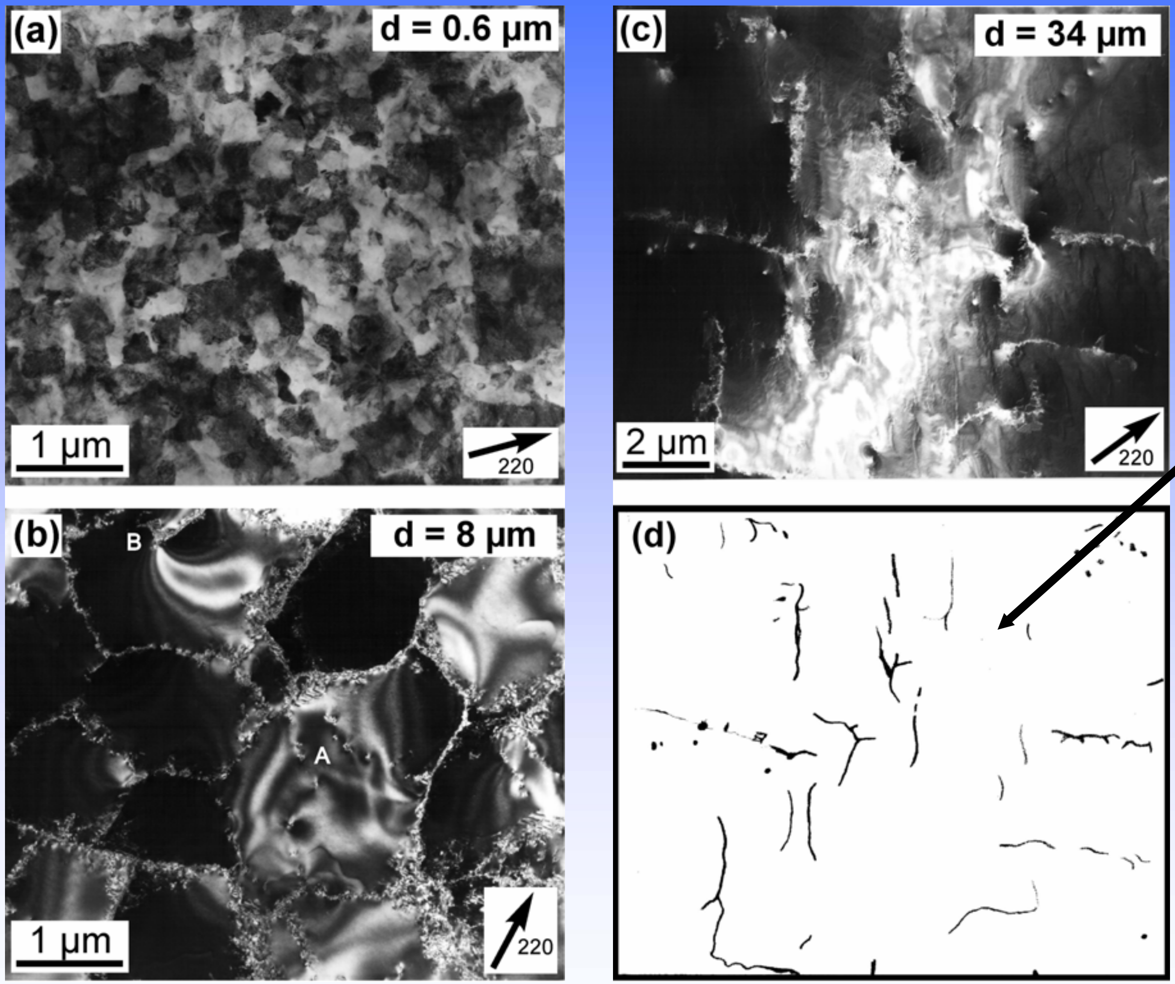
Diamond on silicon





Diamond on Ir/$SrTiO_3$(001)

INTERNAL DEFECT STRUCTURE: TRANSMISSION ELECTRON MICROSCOPY (TEM)



Schematic sketch of defect bands from TEM image in (c)

During textured growth:

closed network of grain boundaries

isolated short defect bands

(quasi single crystal)

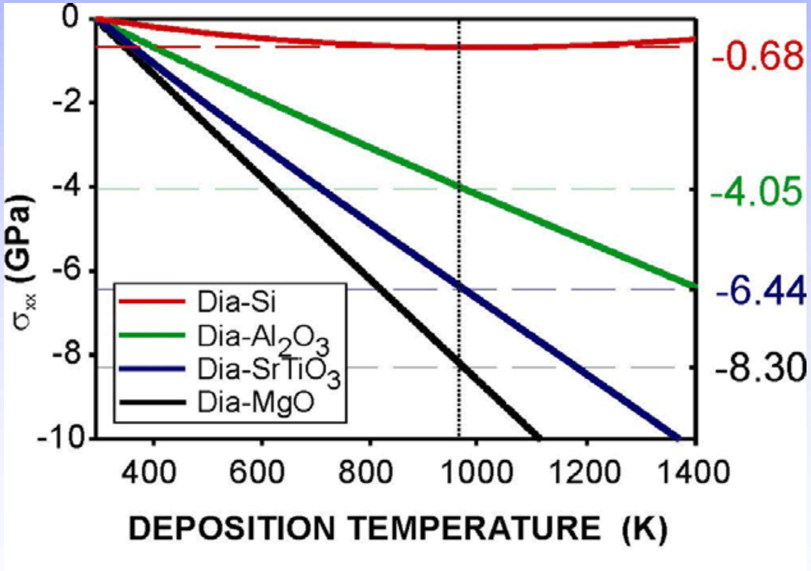
The technological challenge: finding an appropriate multilayer system

OXIDE SINGLE CRYSTALS vs. BUFFER LAYERS ON SILICON

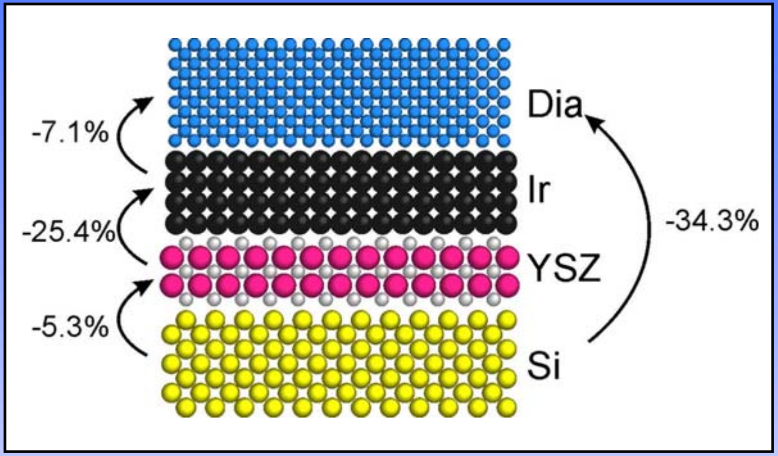
Requirements:

a) Growth of single crystal iridium films

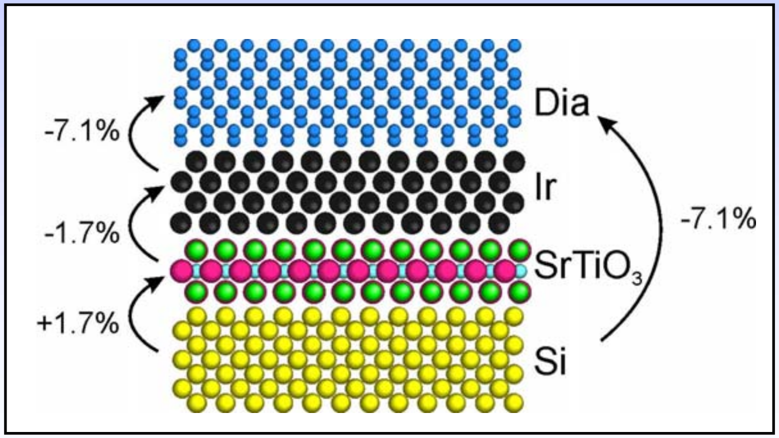
b) Thermally compatible with diamond



Dia/Ir/YSZ/Si(001)



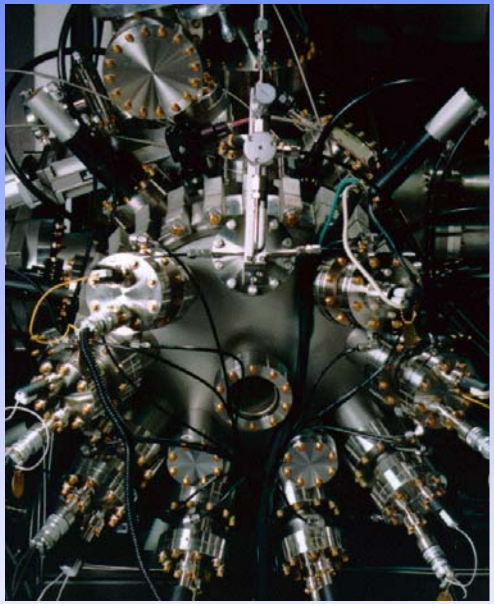
Dia/Ir/$SrTiO_3$/Si(001)



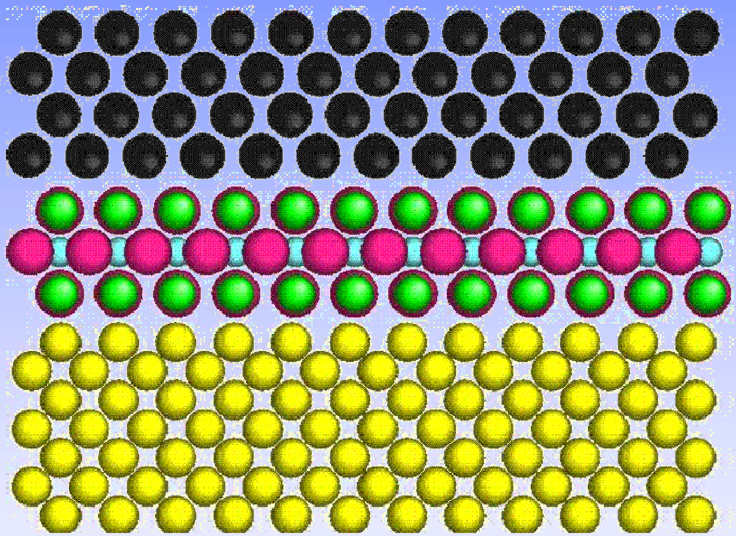
IRIDIUM ON SILICON VIA $SrTiO_3$ BUFFER LAYERS

Epitaxial iridium directly on silicon not possible

→ Oxide buffer layers between silicon and iridium



MBE-System (Prof. D. Schlom, Pennsylvania State University)

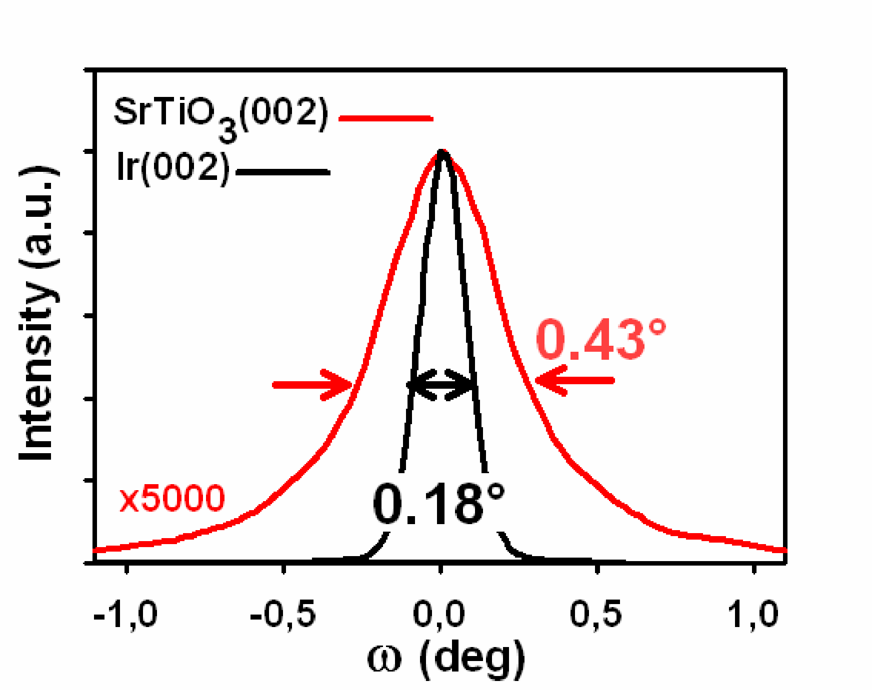


$SrTiO_3$ buffer layer by MBE growth (mosaicity: tilt/twist: 0.43°/1.36°)

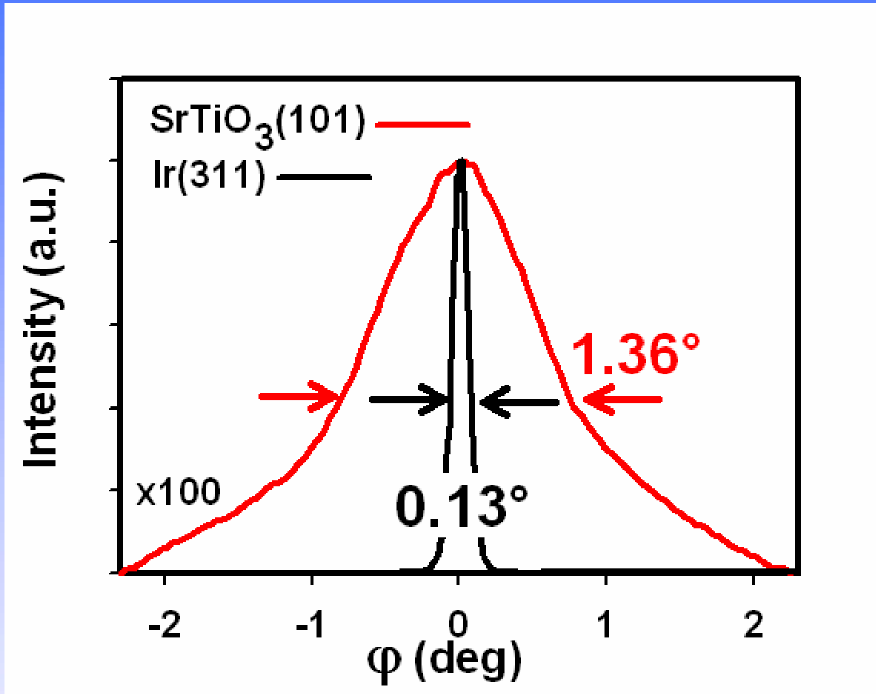
For details: L.V. Goncharova et al., J. Appl. Phys. 100, 014912 (2006)

MOSAIC SPREAD OF THE IR FILMS

Rocking curve



Azimuthal scan



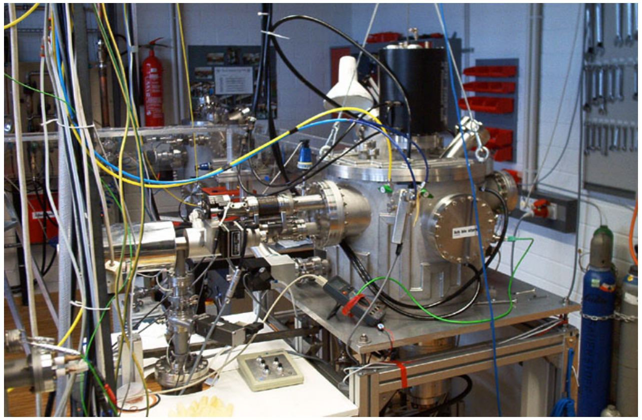
➔Mosaicity (angular spread) of the iridium much lower than that of the underlying oxide buffer layer

Gsell et al., Appl. Phys. Lett., ***91***, *061501(2007).*

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

Pulsed laser deposition (PLD) setup

Laser pulse



KrF excimer laser

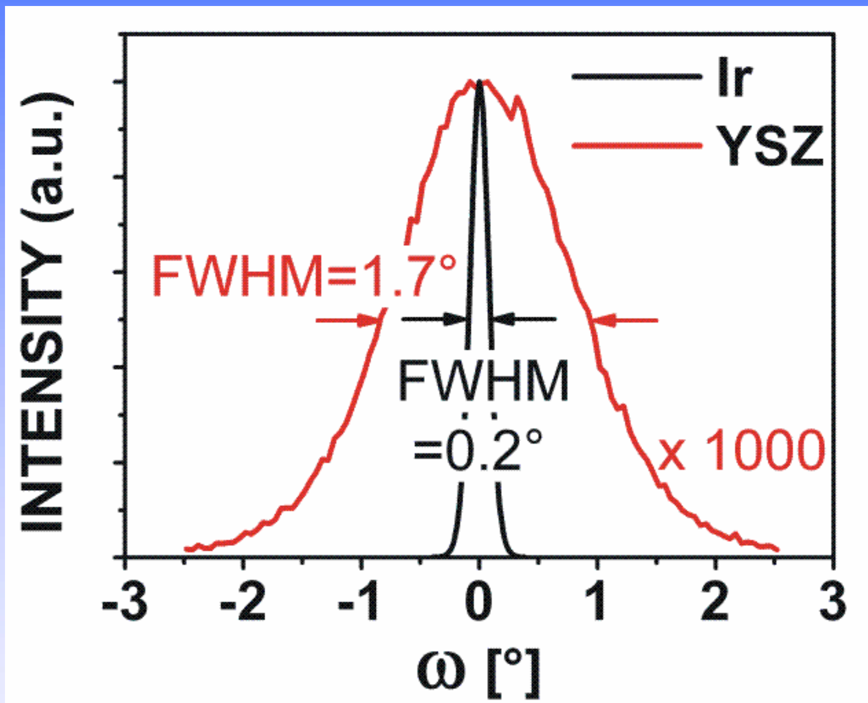
25 ns pulses of 850 mJ

Yttria stabilized zirconia (YSZ) film deposition:

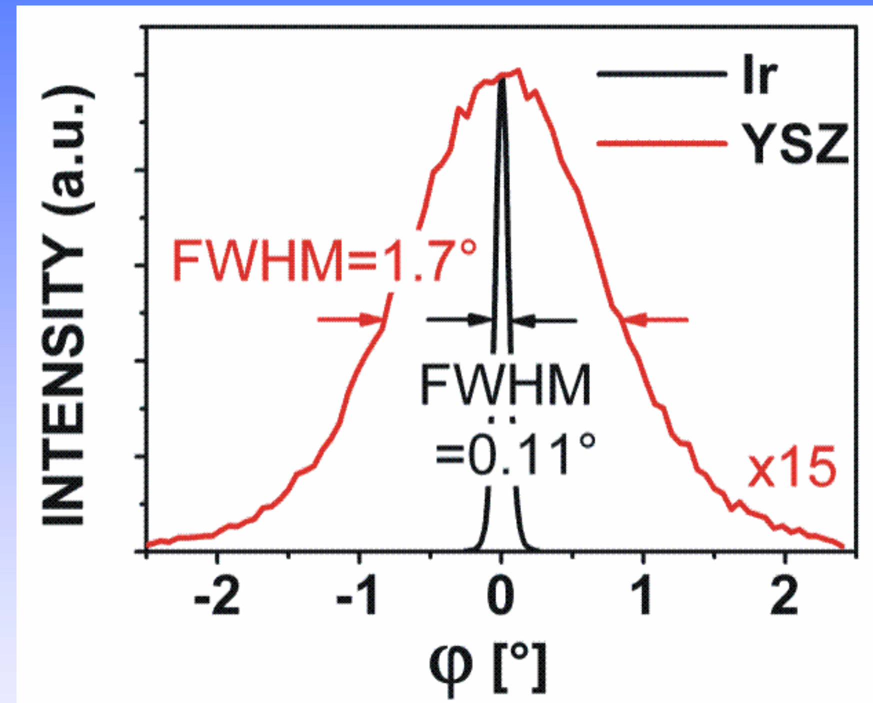
- no removal of the silicon oxide
- ablation target: (ZrO_2) stabilized with Y_2O_3
- 5×10^{-2} Pa oxygen (First 600 pulses without oxygen)
- substrate temperature: 825°C
- thickness: 20 nm (40 nm)

HETEROEPITAXIAL IRIDIUM ON YSZ/Si(001)

Rocking curve

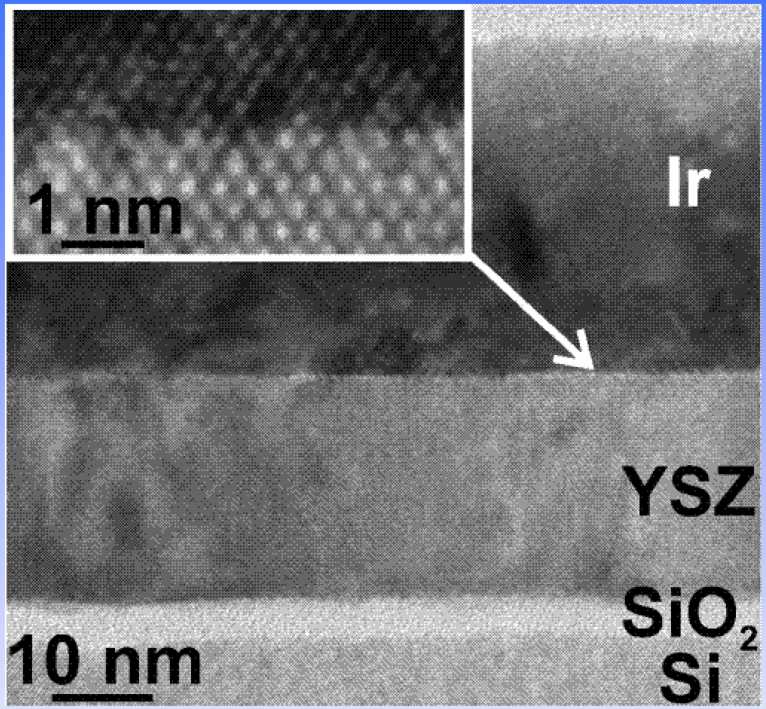


Azimuthal scan



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

MICROSTRUCTURE AND INTERFACE



Cross section TEM micrograph

Dislocation density of iridium: ~10^{11} cm^{-2}

Crystalline interface Ir/YSZ

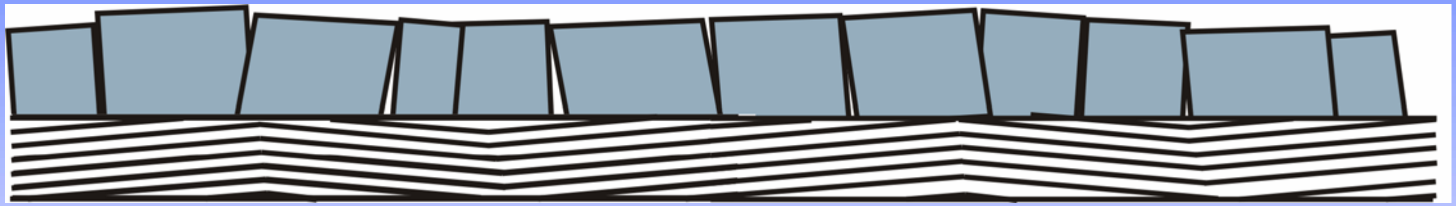
Dislocation density of YSZ: ~10^{12} cm^{-2}

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

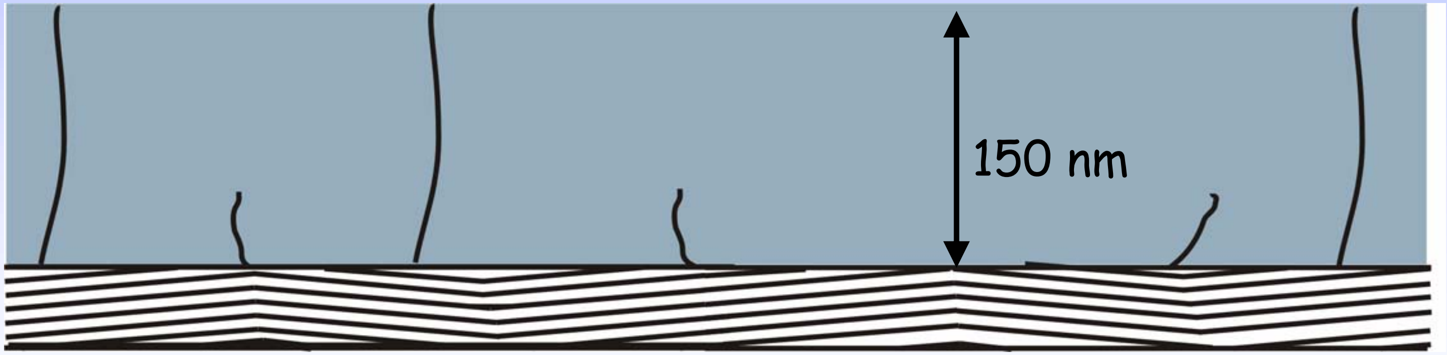
➔Mechanism?

MECHANISM OF TEXTURE IMPROVEMENT DURING IRIDIUM DEPOSITION

Iridium islands on misoriented oxide

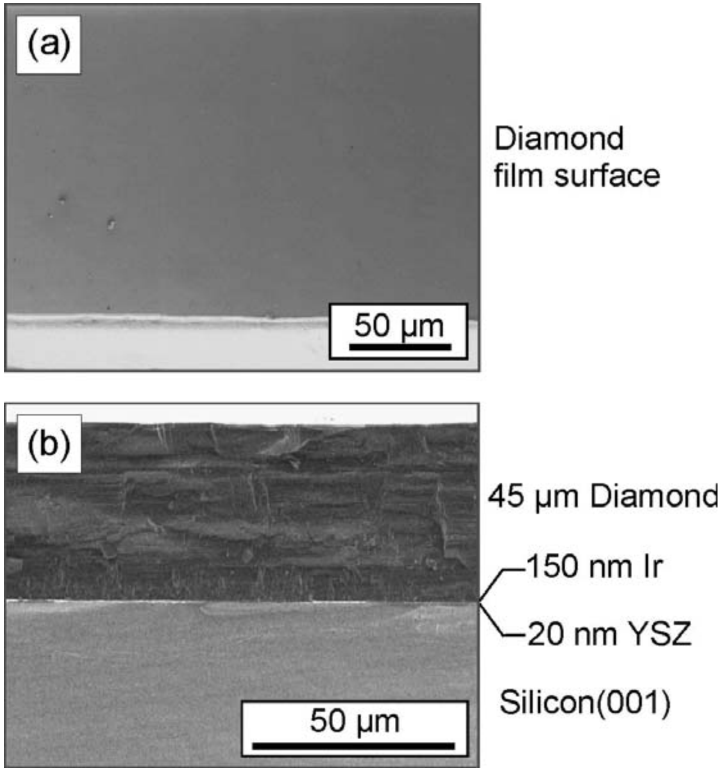


Mechanism I: averaging process during the coalescence of the iridium islands



Mechanism II: burying of defects

THICK DIAMOND FILMS ON Ir/YSZ/Si(001)

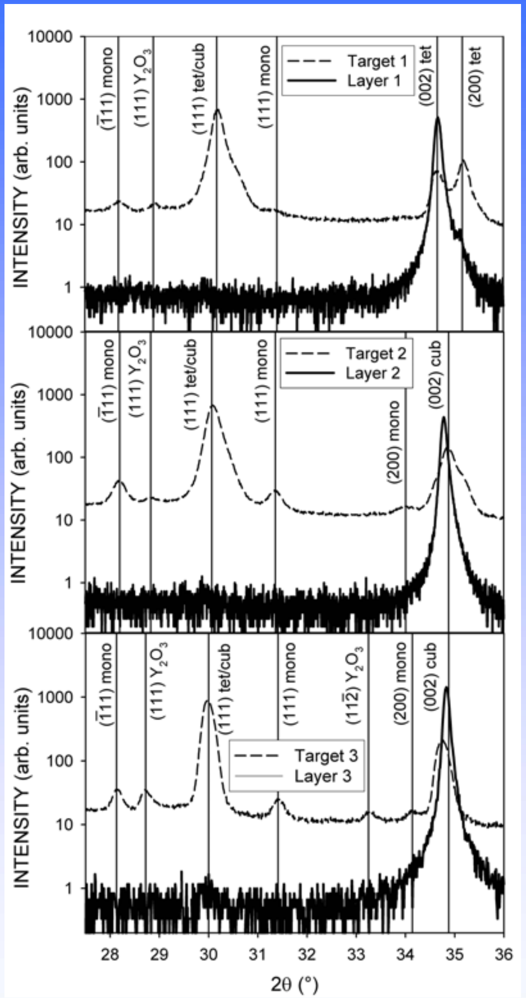


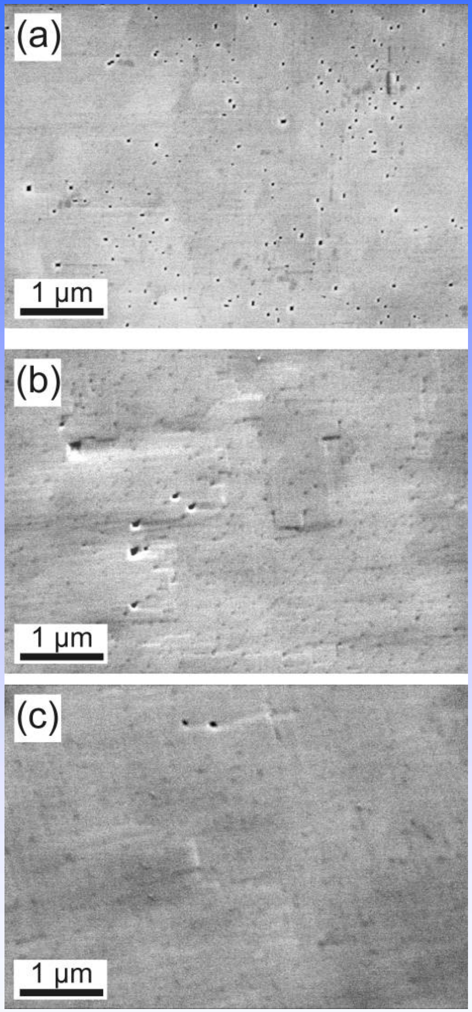
45 µm thick diamond film with good adhesion to the substrate

WHAT IS THE BEST STOICHIOMETRY FOR YSZ BUFFER LAYERS?

2 (of 3) different ablation targets

Laser plume During ablation



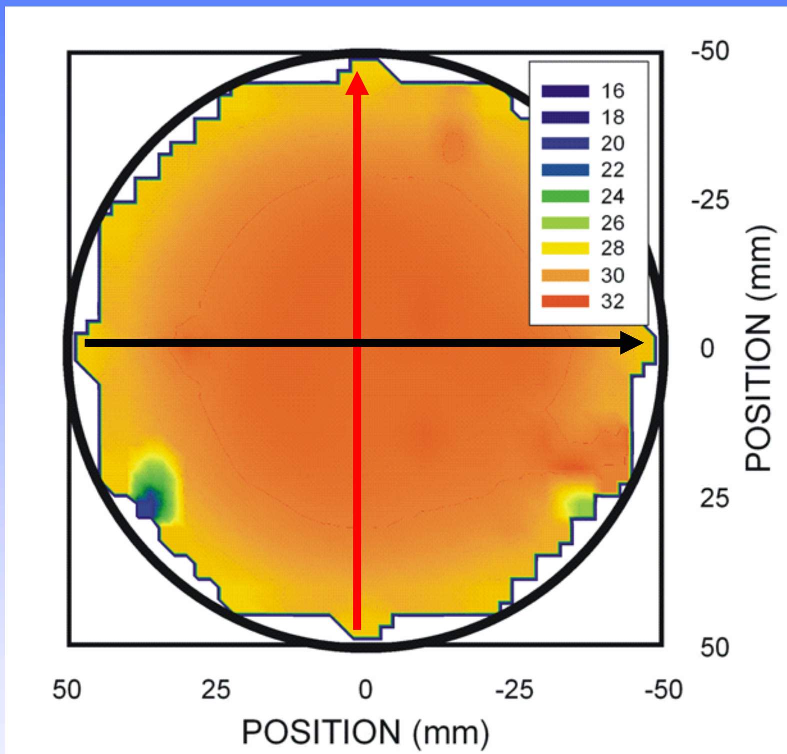


SEM images of Ir surfaces

Tetragonal => cubic YSZ

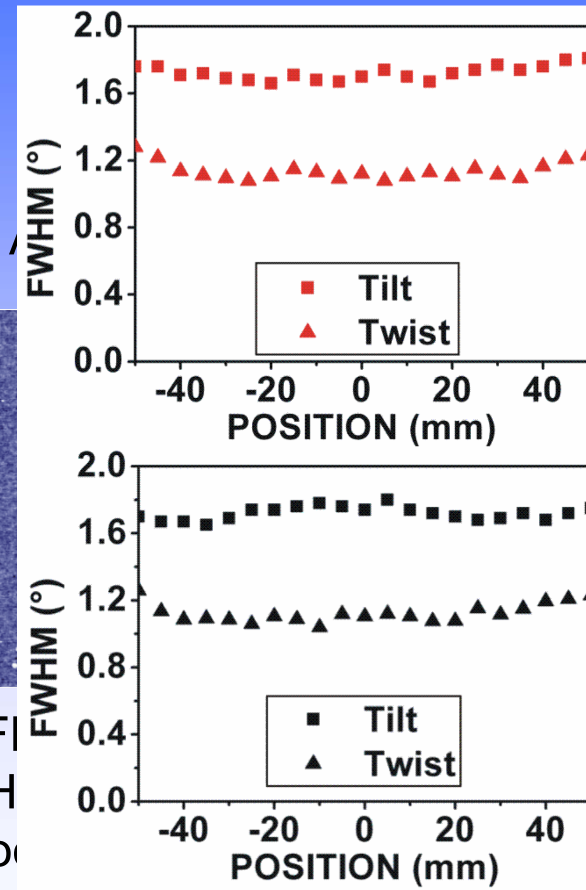
SCALING-UP TO 4": YSZ

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



Homogeneous thickness (10% variation) measured by ellipsometry

XRD



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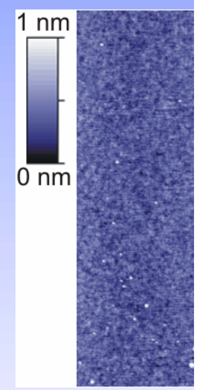

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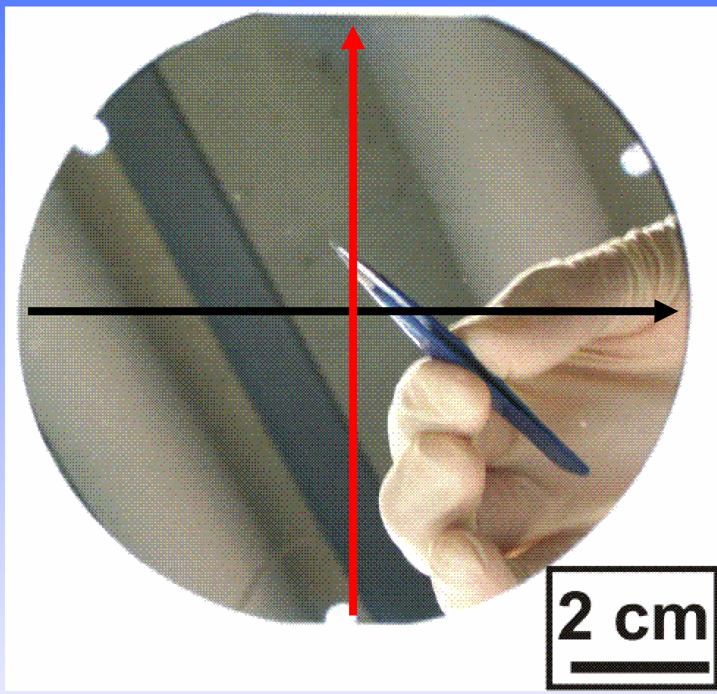
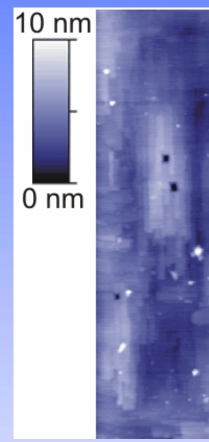
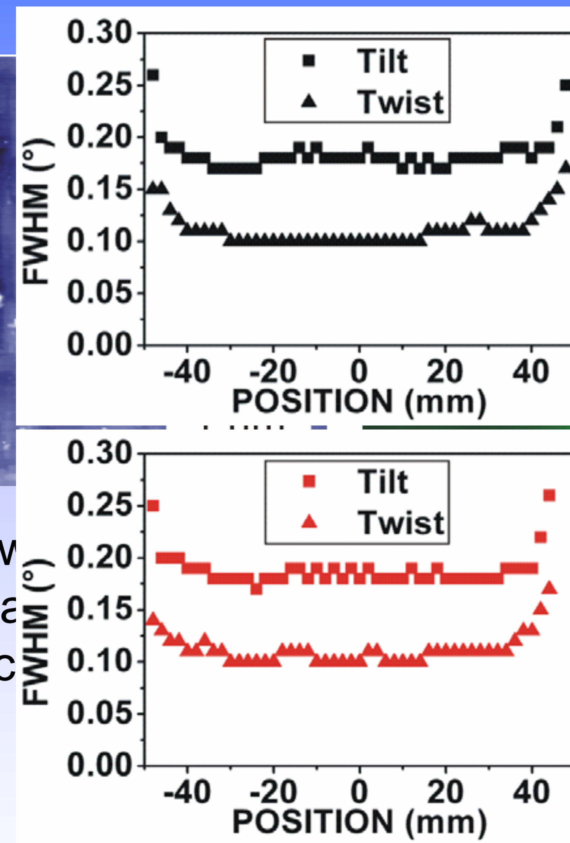
IRIDIUM WAFERS

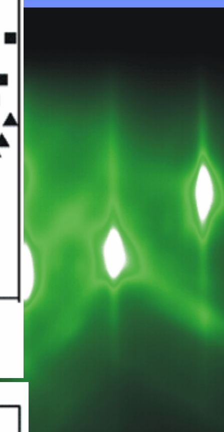
Preparation of the iridium layer by e-beam evaporation on 4-inch YSZ/Si(001) wafers

XRD









AFM: low … es

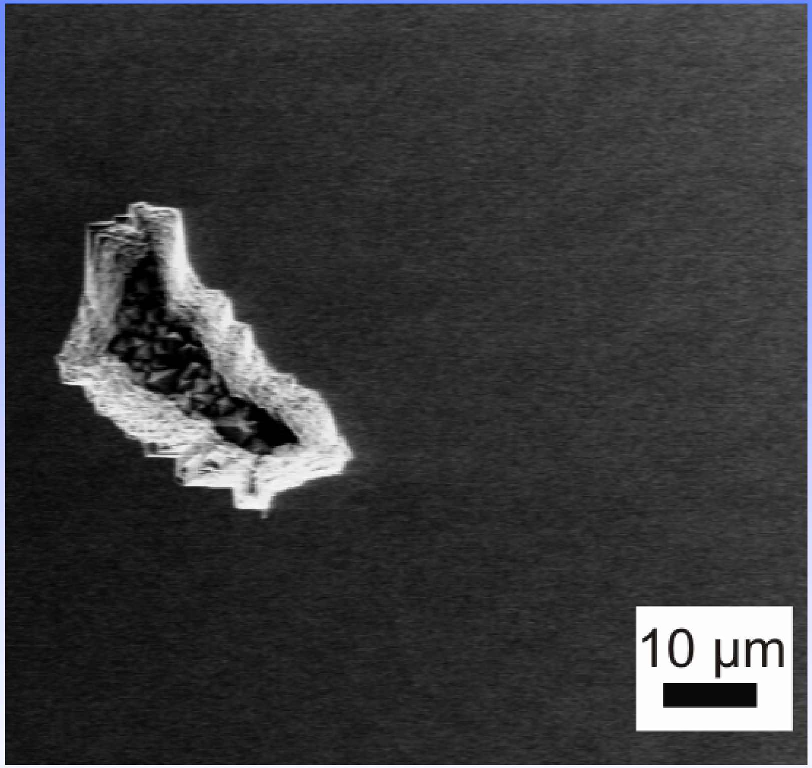
RHEED a…

→ High c … ace

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

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

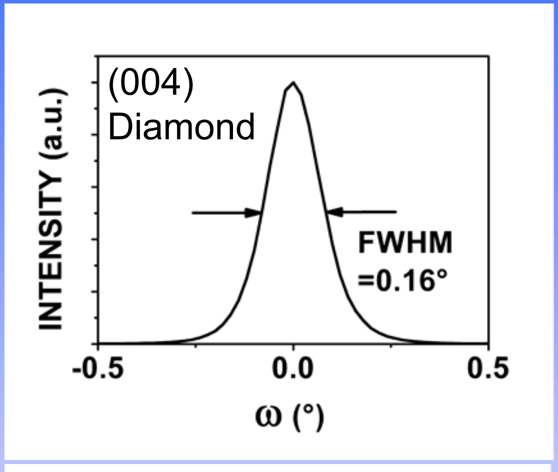
SEM



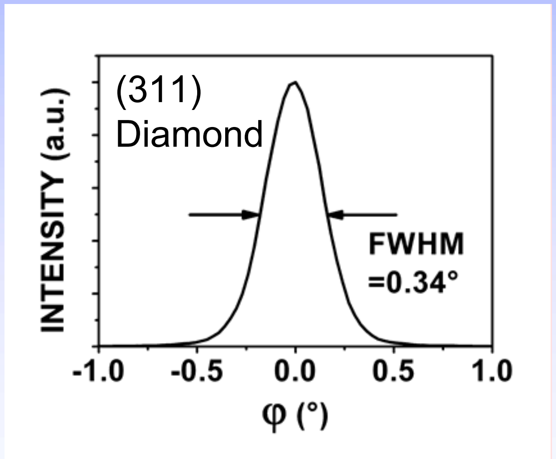
Thickness: 40 µm

XRD

Rocking curve:



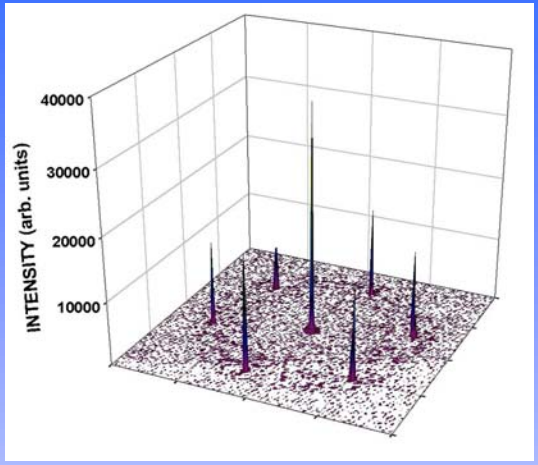
Azimuthal scan:



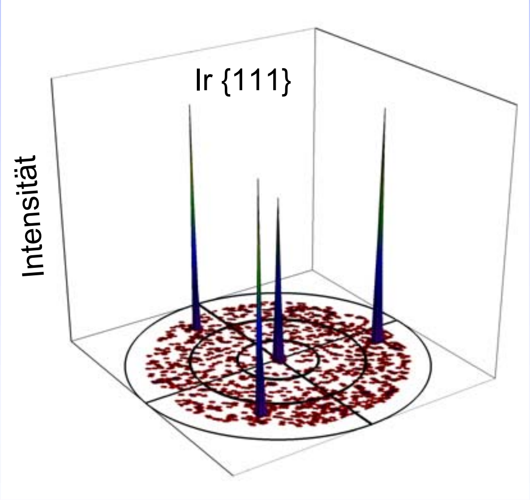
lowest values reported up to now

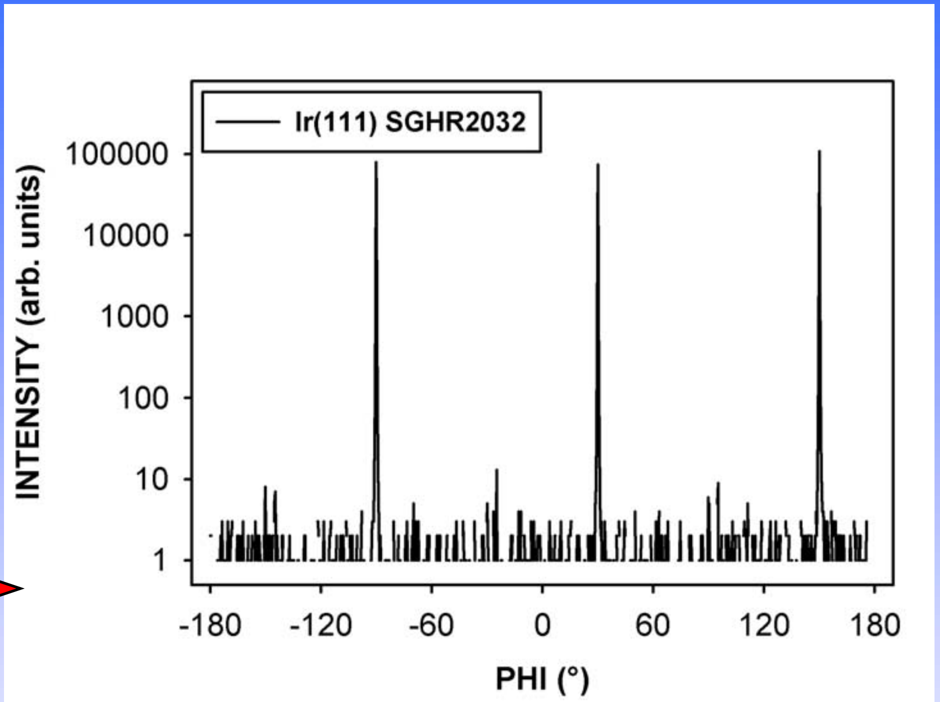
IR(111): EXTREMELY LOW TWINNING RATIO

Ir(111)/Al_2O_3(0001)



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





Twinning < 10^{-4}

Only one texture component

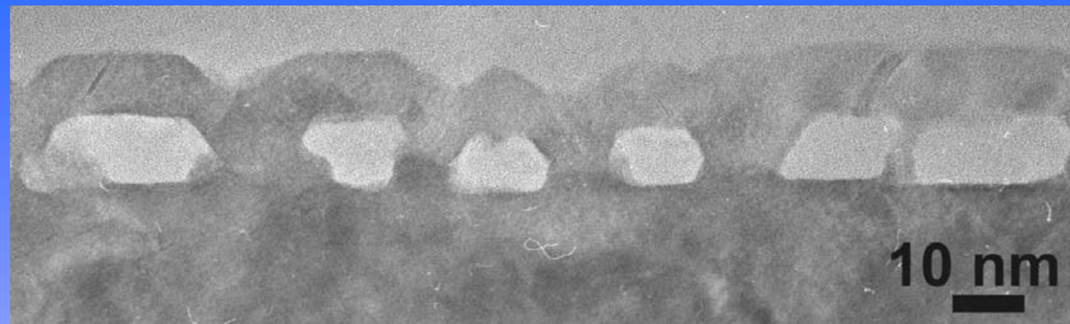
➔ Monocrystalline metal films possible

Why is Ir so much better than any other substrate?

=> Understanding BEN on Ir

SPECIAL FEATURES OF DIAMOND ON IRIDIUM

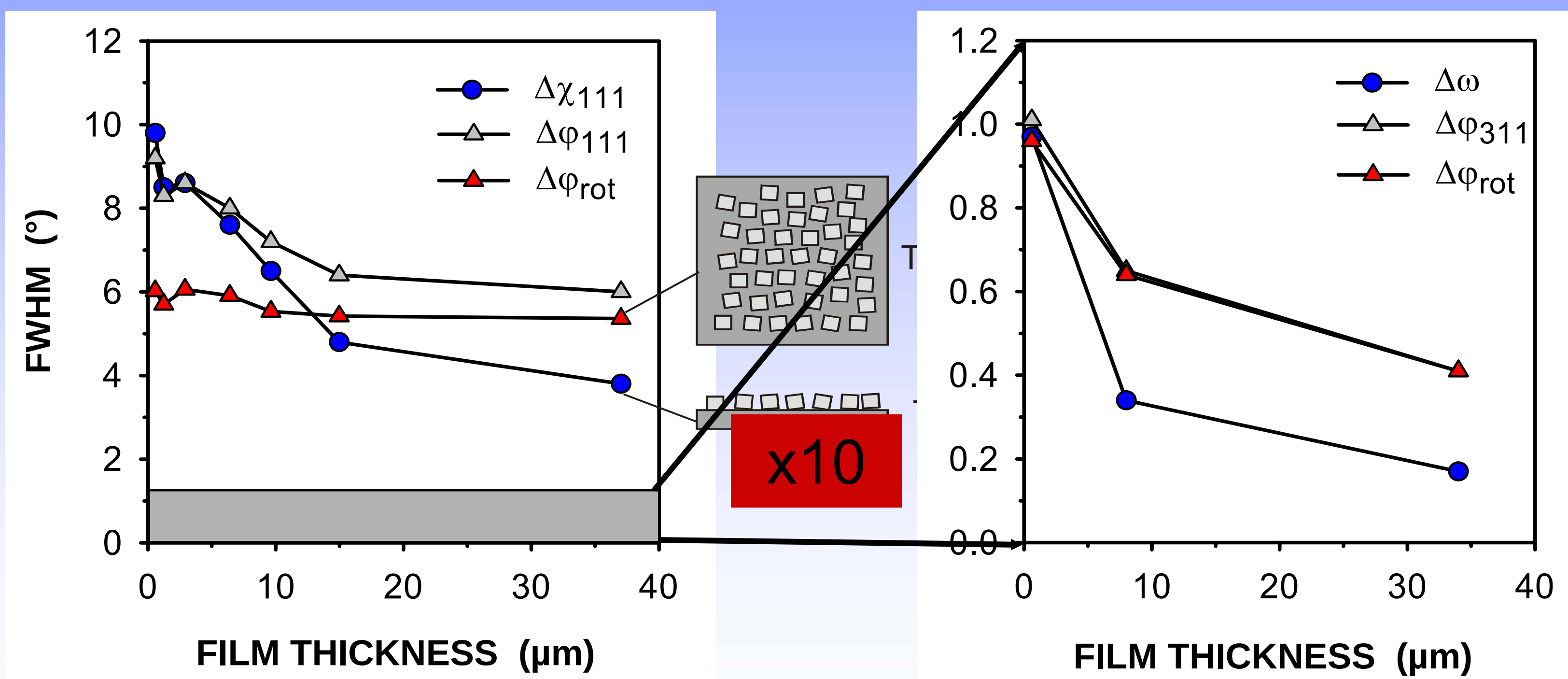
Highest density of oriented grains



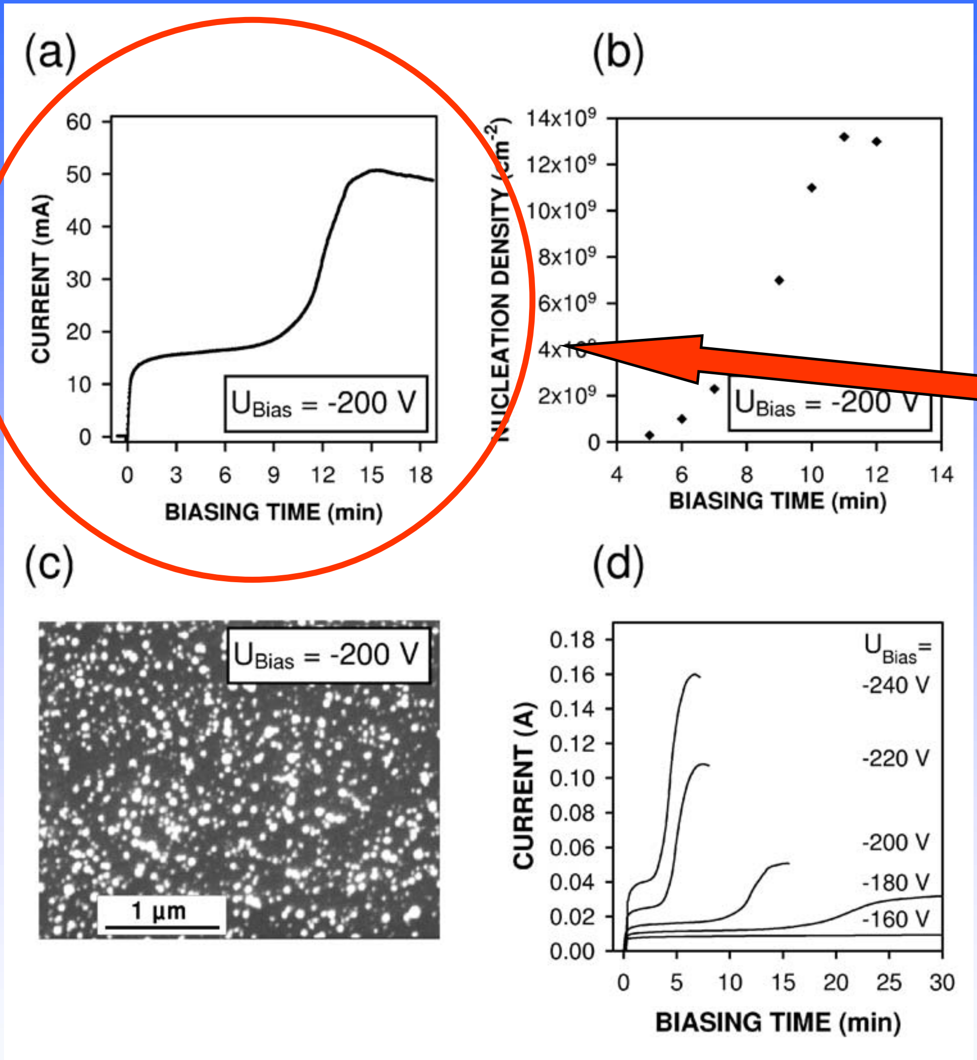
Cross section TEM image after 2 min growth

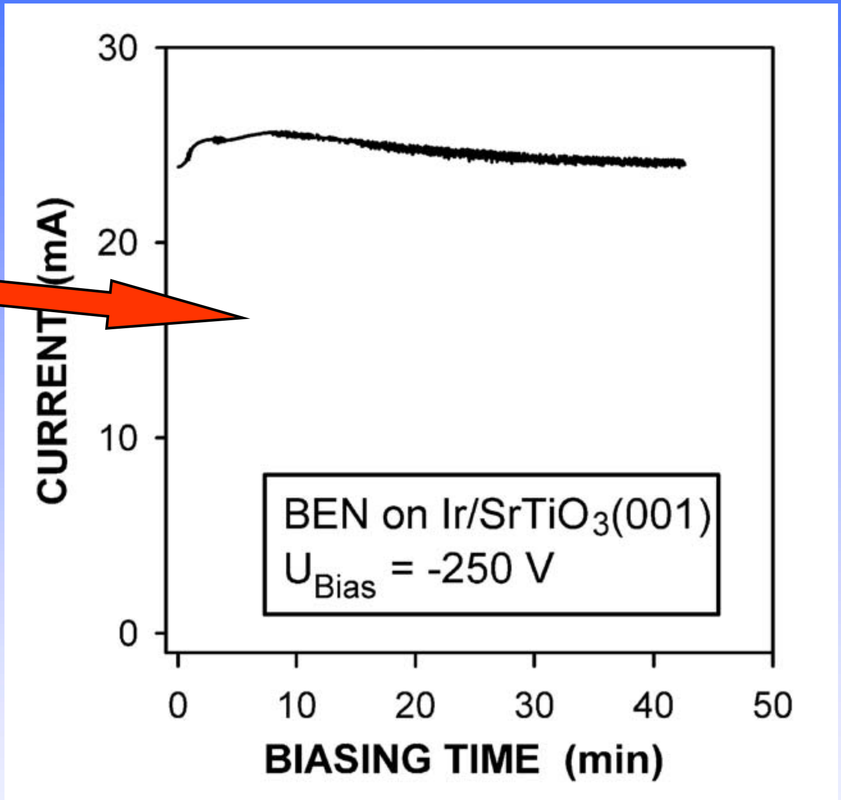
Dia/Si(001)

Dia/Ir/$SrTiO_3$(001)



NUCLEATION ON SILICON vs. IRIDIUM

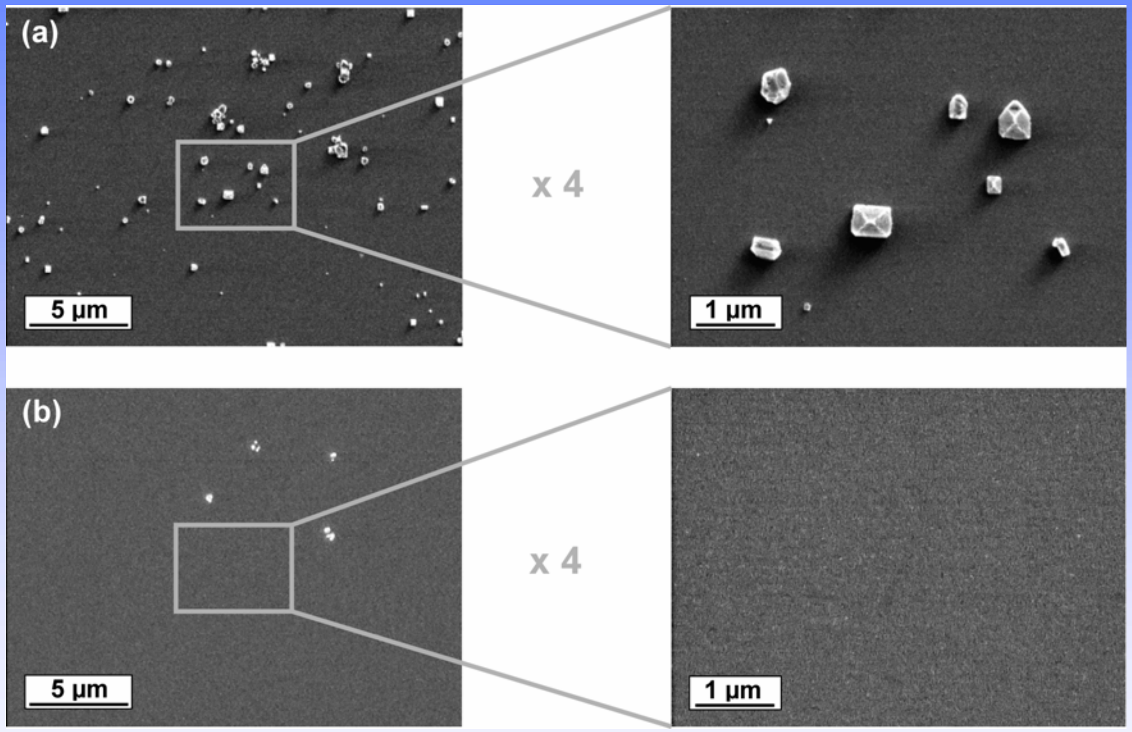




THE FATE OF DIAMOND GRAINS UNDER THE BIAS ENHANCED NUCLEATION CONDITIONS ON IRIDIUM

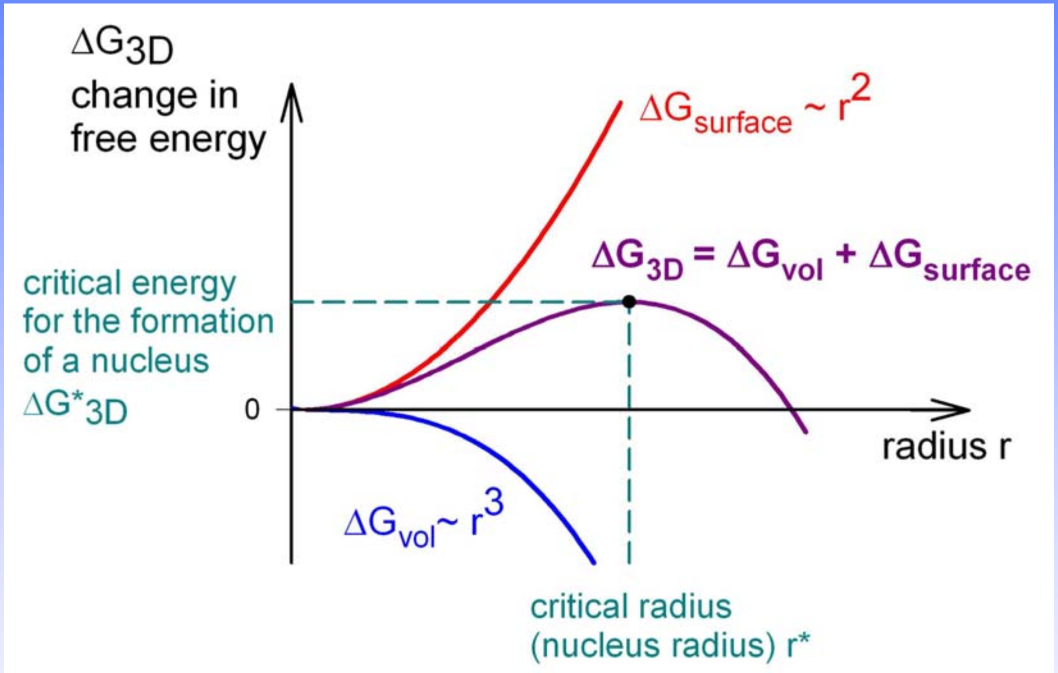
before BEN

after 60 min BEN



Diamond nucleation occurs under conditions under which diamond grains are etched!!!

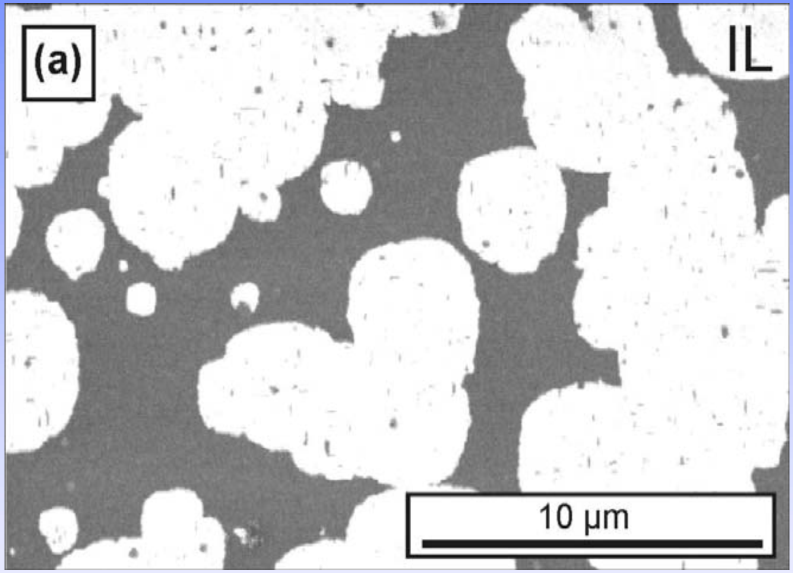
CLASSICAL NUCLEATION THEORY



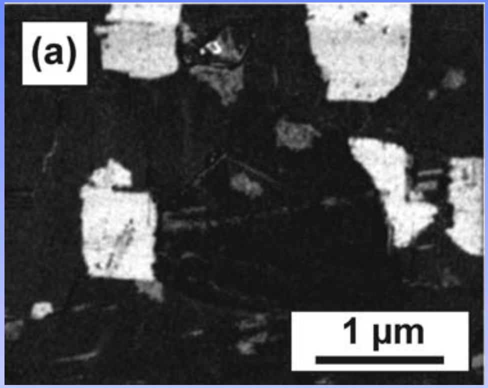
Nucleation under etching conditions contradicts classical nucleation theory

THE IRIDIUM SURFACE AFTER BEN

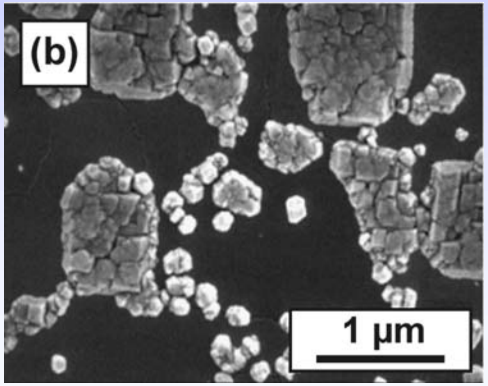
Bright domains in the SEM



Correspondence
Domains ←→ Diamond islands??

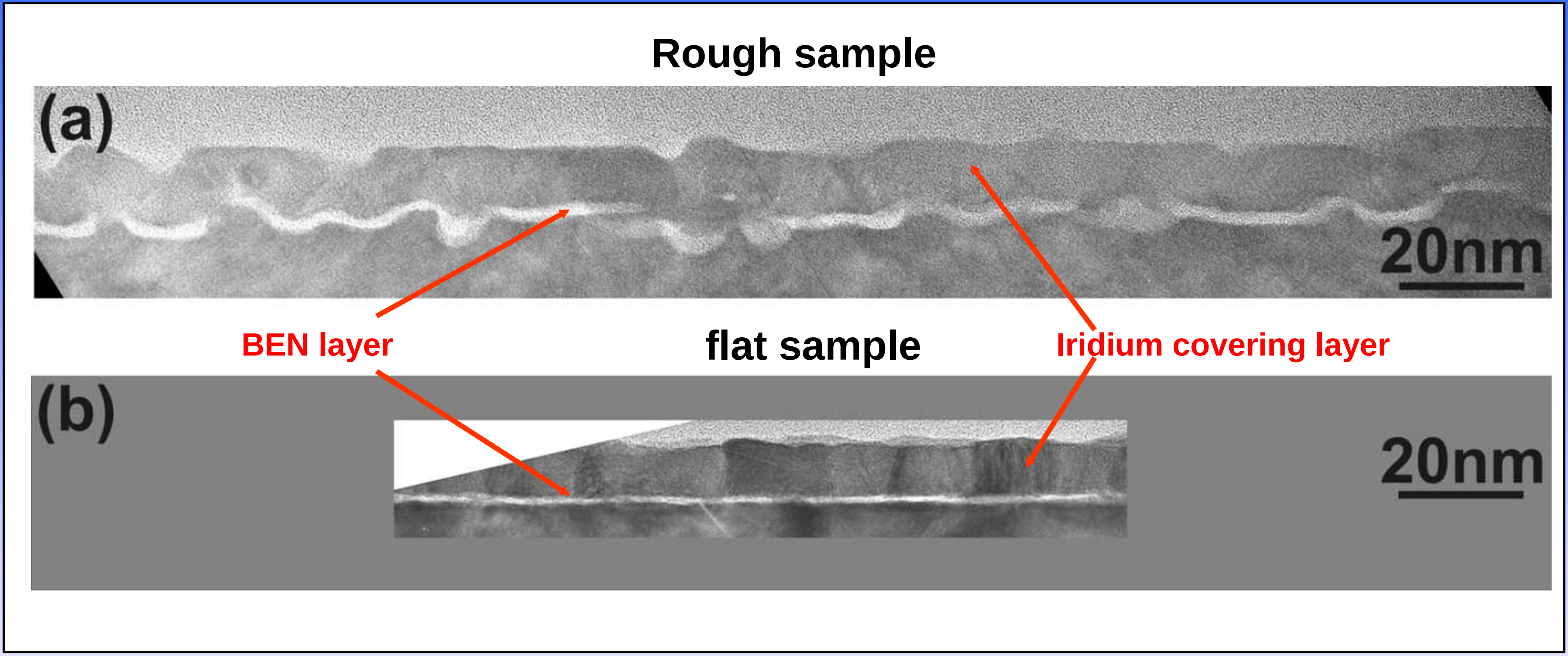


Growth step 1 year later



What is the amount of carbon at the Ir surface after BEN?

CROSS SECTION TEM IMAGES OF BEN SAMPLE 1 & 2



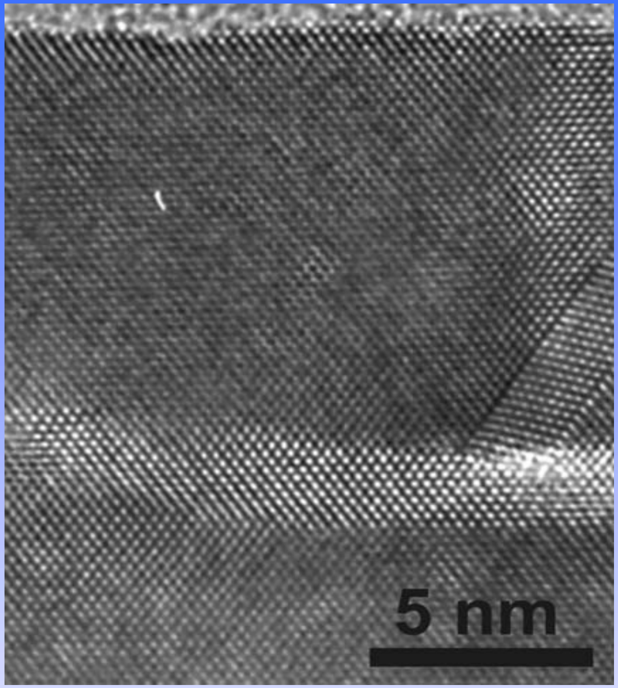
➔ **A slit is clearly visible**

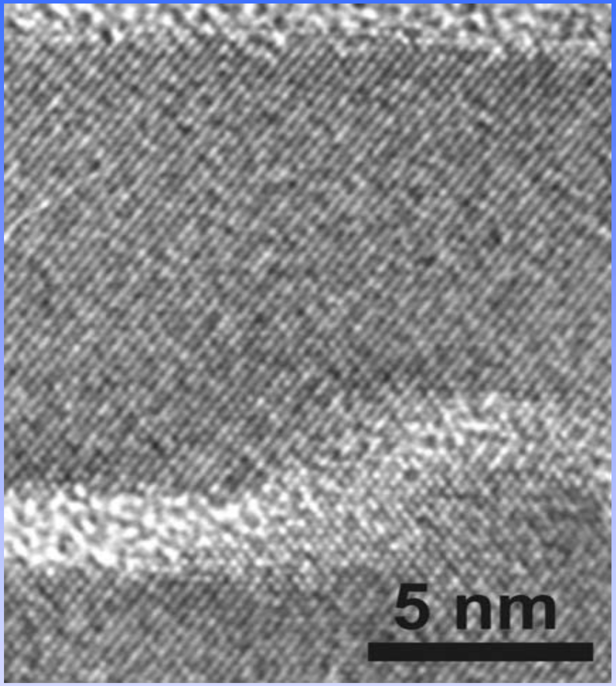
➔ **On the flat sample: continuous with rather homogeneous thickness**

➔ **Thickness: ~ 1 nm**

The internal structure of the BEN layer?

HIGH RESOLUTION IMAGES OF THE INTERFACE REGION (FLAT & ROUGH SAMPLE)





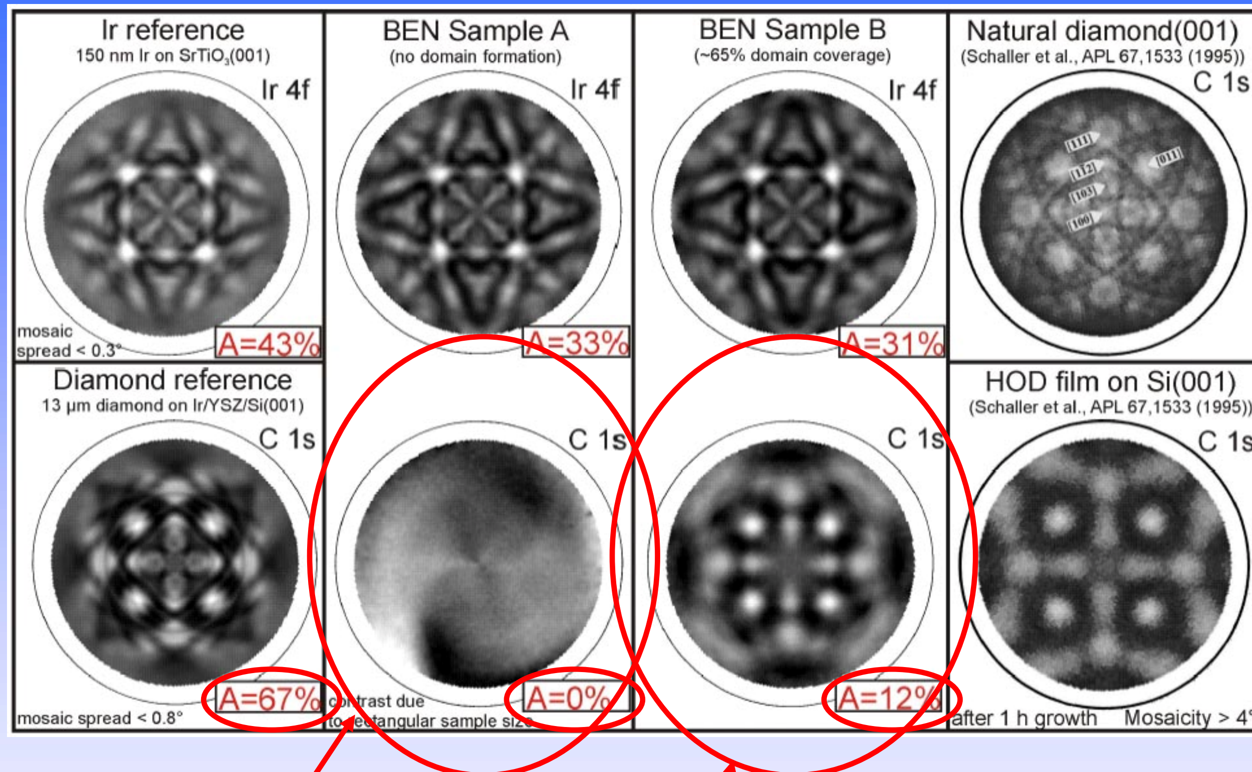
➔ Epitaxial iridium covering layer (preferentially on rough sample)

➔ 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)

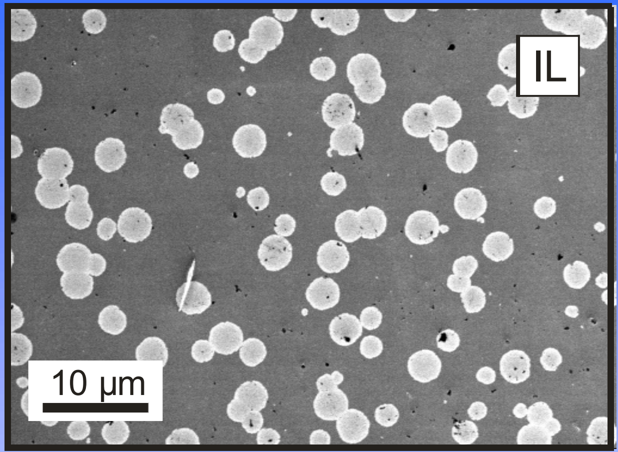


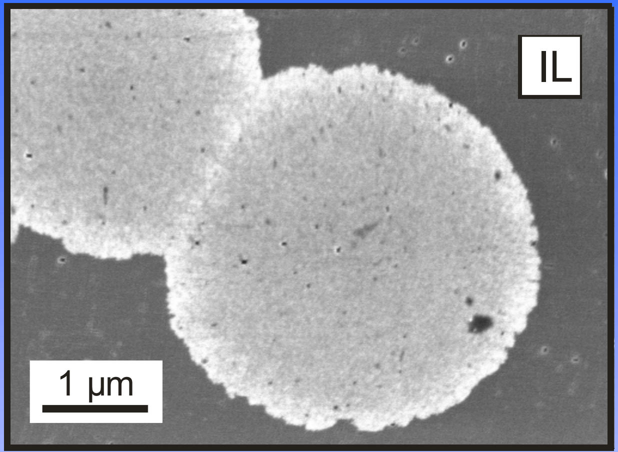
- no XPD C1s pattern in case of unsuccessful nucleation
- XPD C1s pattern similar to highly oriented polycrystalline diamond in case of successful BEN
- anisotropy values ➔ compatible with diamond grains of 10 nm lateral size !!??

The topographic signature of the domains?

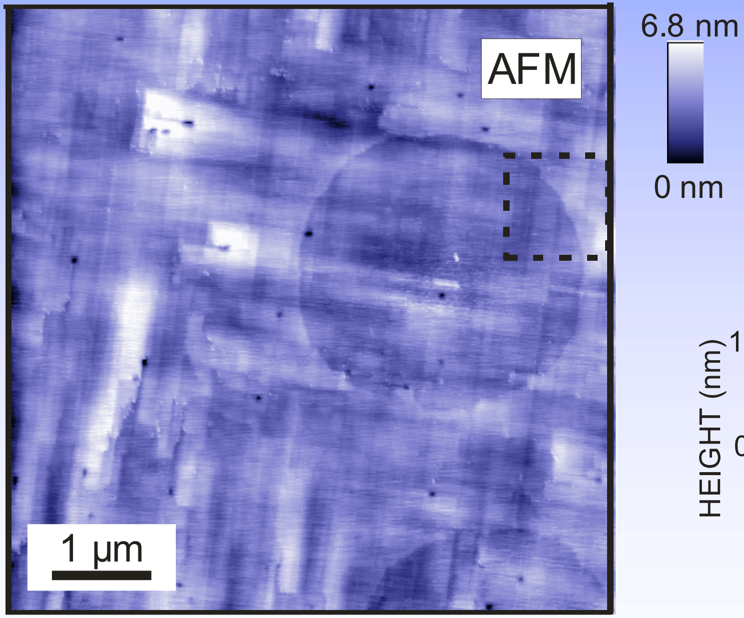
TOPOGRAPHIC SIGNATURE OF THE DOMAINS

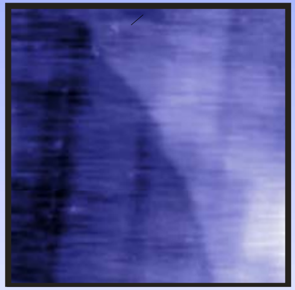
SEM



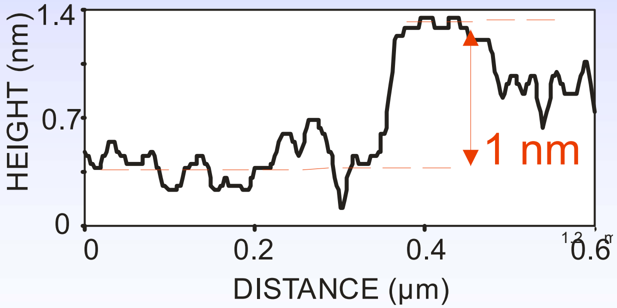


Nucleation in a pure DC discharge



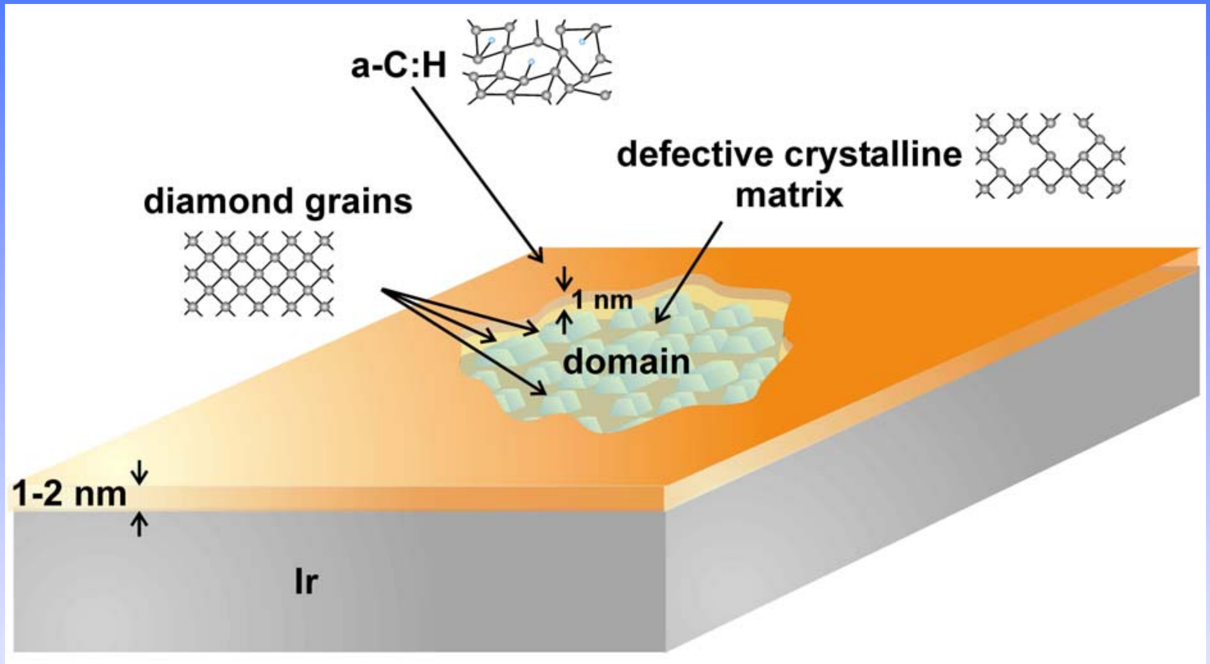


MEAN STEP HEIGHT:
1.1 ± 0.1 nm



AFM

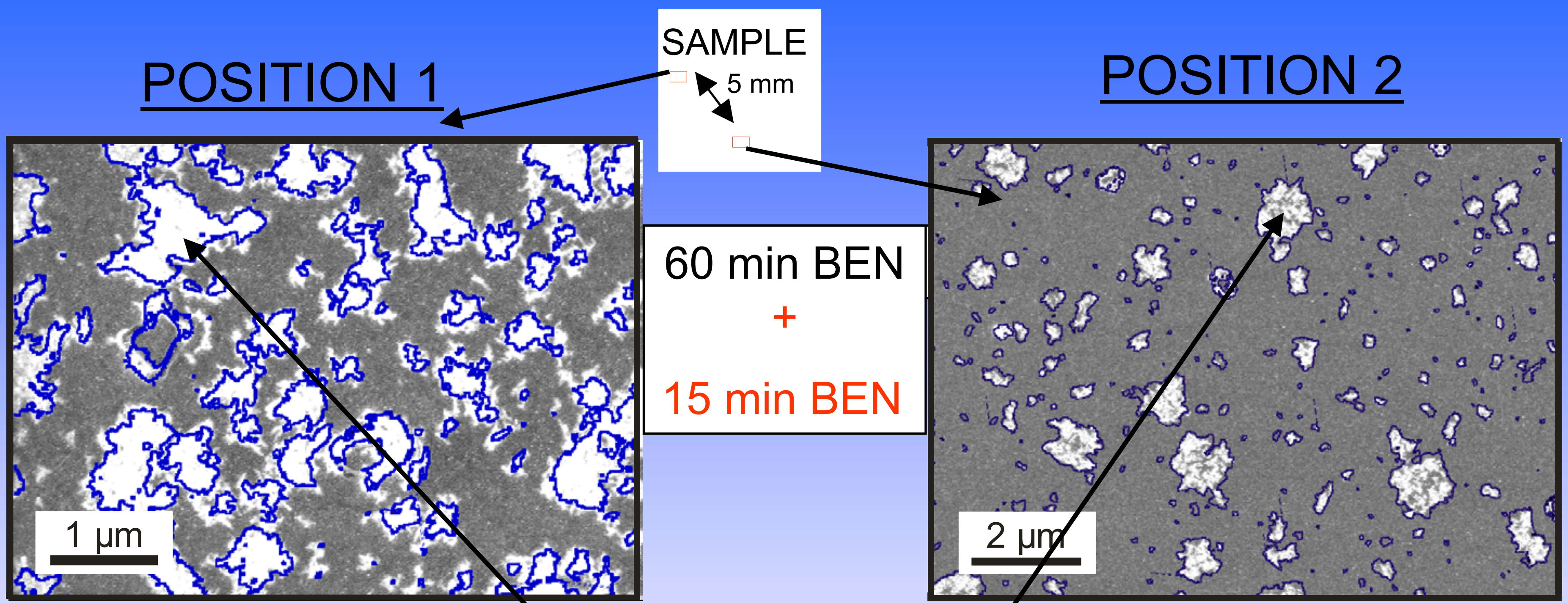
A MODEL DESCRIBING THE STRUCTURE OF THE BEN LAYER INCLUDING THE DOMAIN



- 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?

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
- **$SrTiO_3$ 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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