

NoRHDia- Workshop
August 30 – September 1, 2005
GSI, Darmstadt

CURRENT STATE OF HETEROEPITAXIAL DIAMOND DEPOSITION

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OUTLINE

- Different approaches for the realization of large area single crystal diamond
- Heteroepitaxy and bias enhanced nucleation (BEN)
- Search for the appropriate substrate
- Iridium buffer layers: a gift of nature
- Structure improvement by textured growth
- How to realize large area iridium layers on silicon
- Current status and future challenges
- Summary



HOMOEPITAXIAL DIAMOND GROWTH

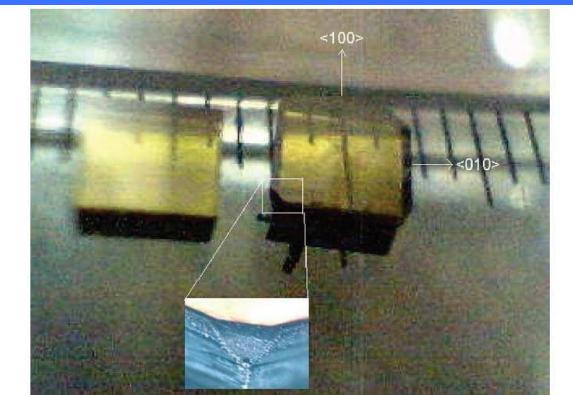


Fig. 1. Photograph of seed and as-grown unpolished CVD diamond and a magnification of CVD-diamond corner. The (100) direction corresponds to the four sides of the diamond cube.

Growth rate with N_2 : 150 $\mu\text{m}/\text{h}$

Yan, Vohra, Mao, Hemley, Proc. Natl. Acad. Sci.
USA 99 (2002) 12523.

Other groups:

Tranchant, Saclay

A. Gicquel, R. Sussmann LIMHP-CNRS, Paris

R.B. Jackman, University College London

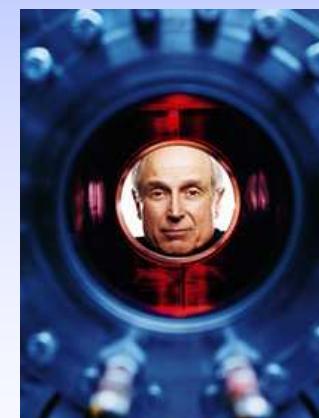
N. Fujimori, AIST, Tsukuba, Japan

.....

Companies:

Apollo Diamond (USA)

Element Six



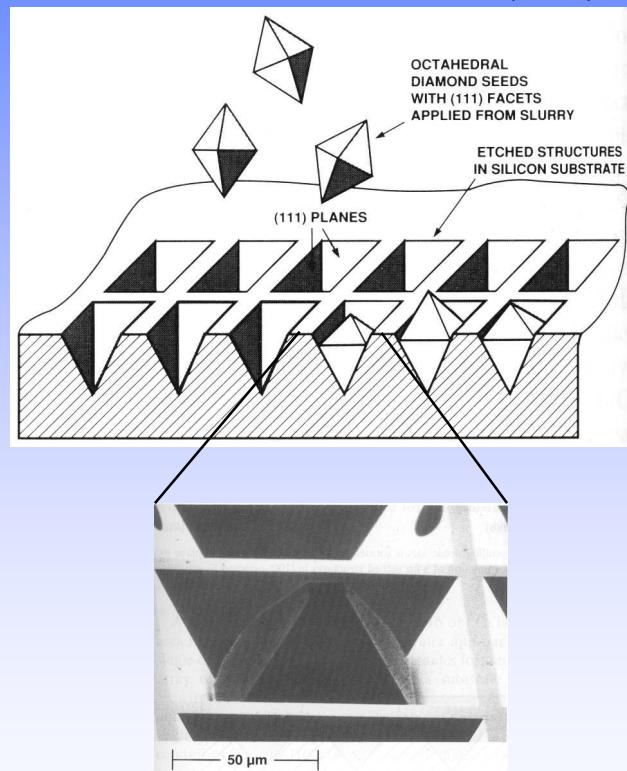
WIRED (Sept. 2003)
Linares (Apollo).... the company is producing 10-millimeter wafers but predicts it will reach an inch square by year's end and 4 inches in five years.



ROUTES TO SINGLE CRYSTAL DIAMOND LAYERS: FORMER ATTEMPTS

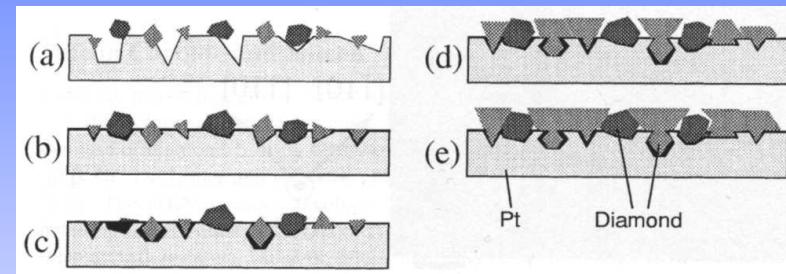
Patterned Si-substrates + macroscopic seed crystals

M.W. Geis, Diamond Relat. Mater. 1 (1992) 684

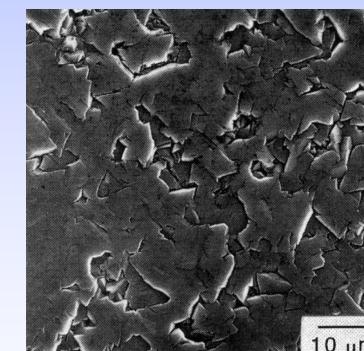


Single crystal metal surface (e.g. Pt) + nanocrystalline seed crystals

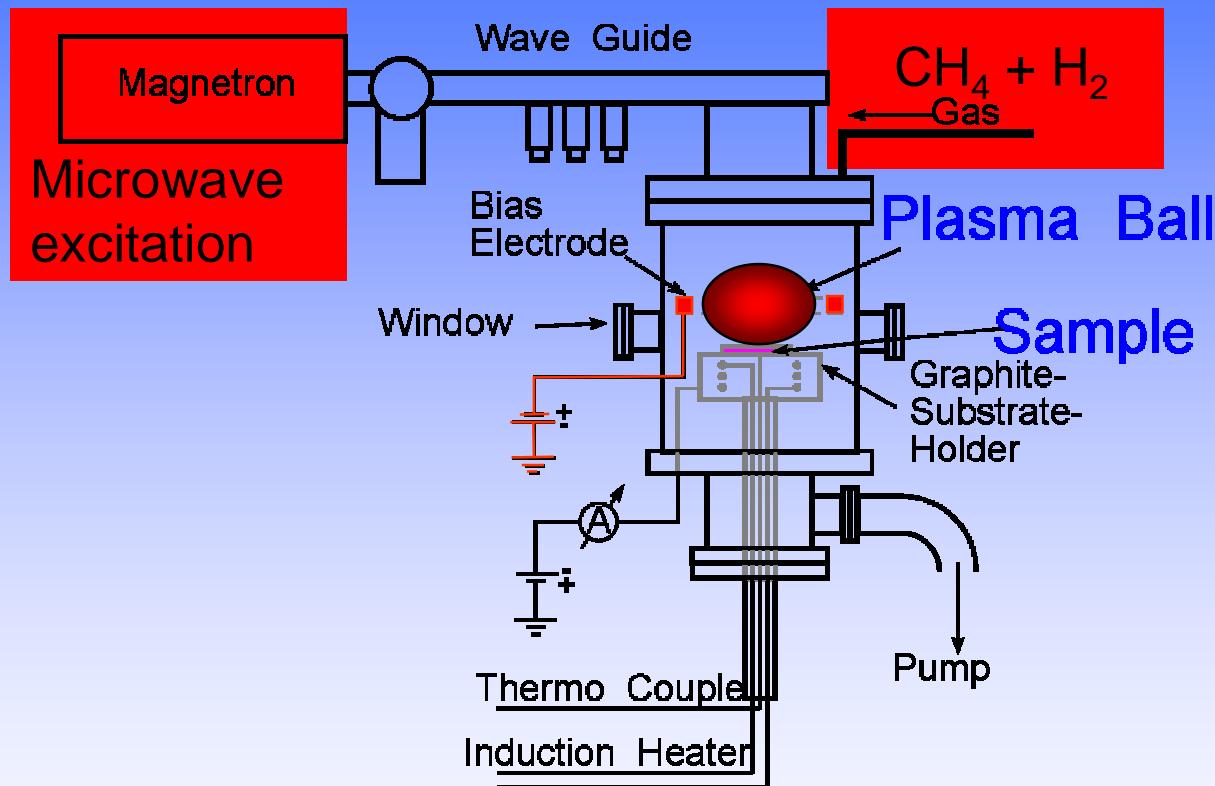
Principle (schematic)



**Diamond on Pt(111)
SEM-image**



OUR SETUP



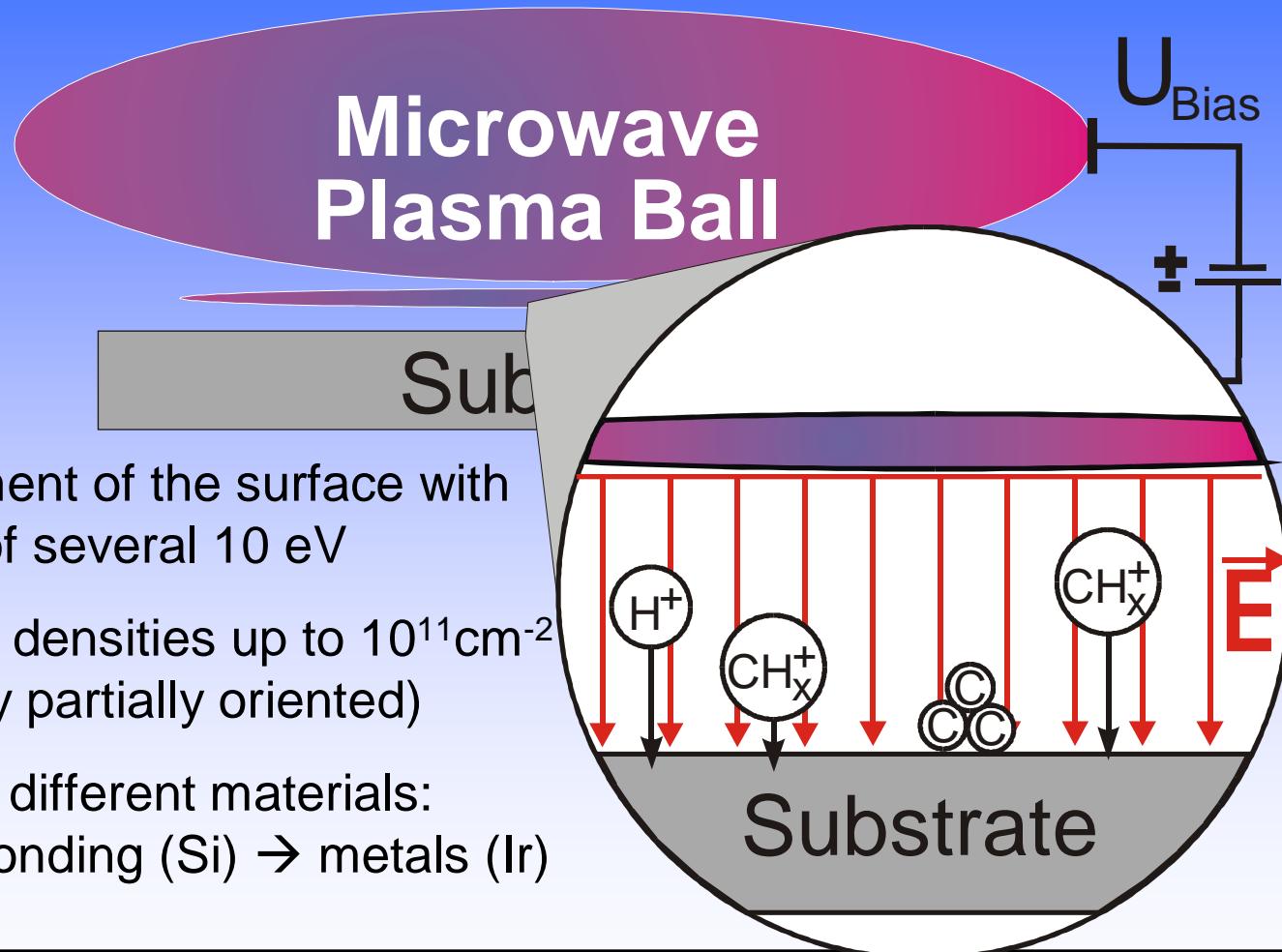
BIAS ENHANCED NUCLEATION (BEN)

Microwave
plasma ball

Substrate

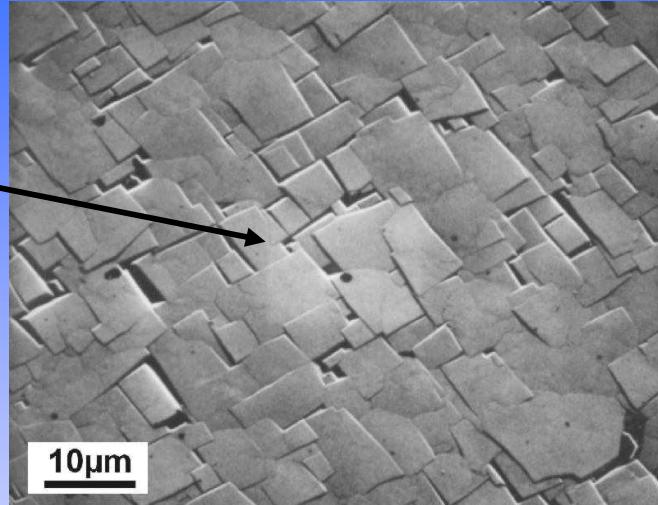


BIAS ENHANCED NUCLEATION (BEN)



EPITAXIAL DIAMOND FILMS ON Si(001)

Surface:
coplanar,
azimuthally
oriented {001}-
facets



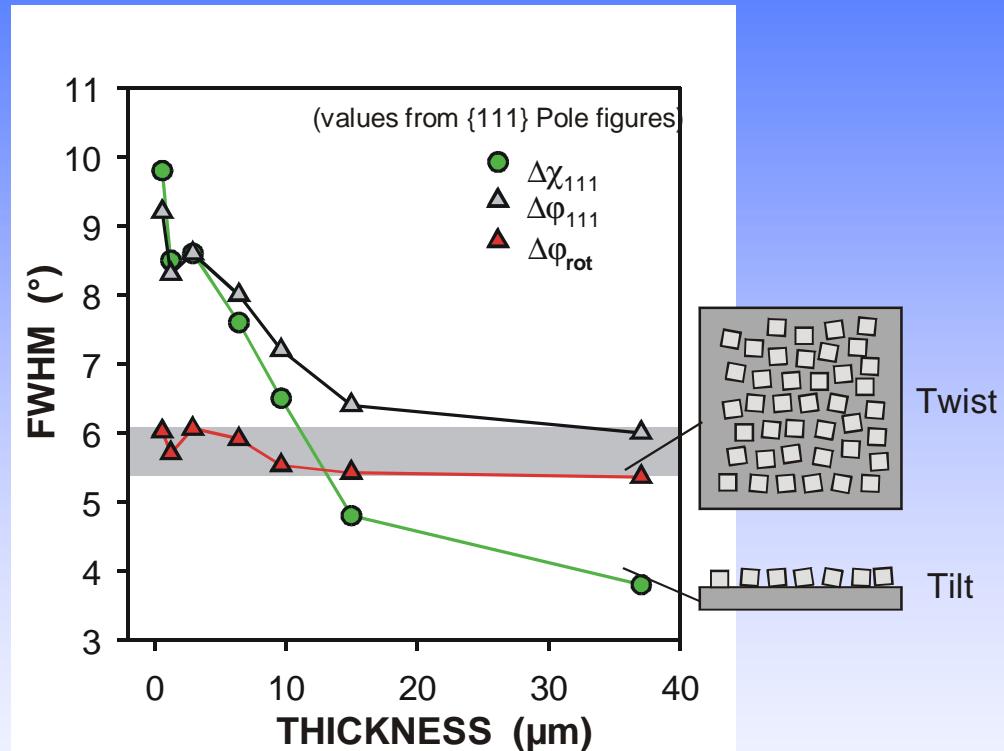
cross section:
columnar growth



grain coarsening



IMPROVEMENT BY TEXTURED GROWTH: TILT AND TWIST



Results:

Tilt can be reduced drastically

Twist is nearly constant

→ Limitation for film optimization by textured growth

Minimum value for Twist: $\sim 3.9^\circ$

Up to now all epitaxial layers on silicon remained polycrystalline



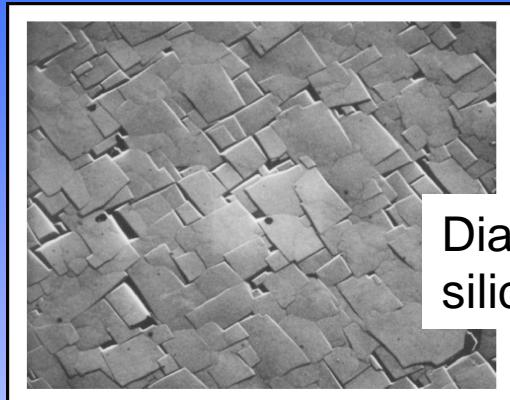
WHY IRIDIUM?

	Light platinum metals			Heavy Platinum metals				
Atomic number	44	45	46	76	77	78	14	
Element	Ru	Rh	Pd	Os	Ir	Pt	Si	$\beta\text{-SiC}$
M.P. (°C)	2334	1964	1555	3033	2446	1768	1412	2830
Expansion coefficient (10^{-6}K^{-1})	6.4	8.2	11.8	5.1	6.4	8.8	2.6	2.77
Density (g/cm^3)	12.1	12.4	12.0	22.59	22.5	21.5	2.33	3.17
Crystal system	hexagonal	cubic	cubic	hexagonal	cubic	cubic	cubic	cubic
Lattice constant (nm)	$a_0=0.27058$ $c_0=0.42816$	0.38032	0.38903	$a_0=0.27341$ $c_0=0.43918$	0.38392	0.39236	0.54310	0.43596
Misfit with diamond (%)		6.6	9.1		7.6	10	55.2	22.2



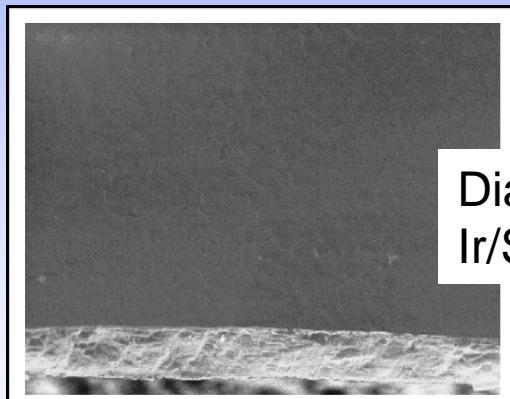
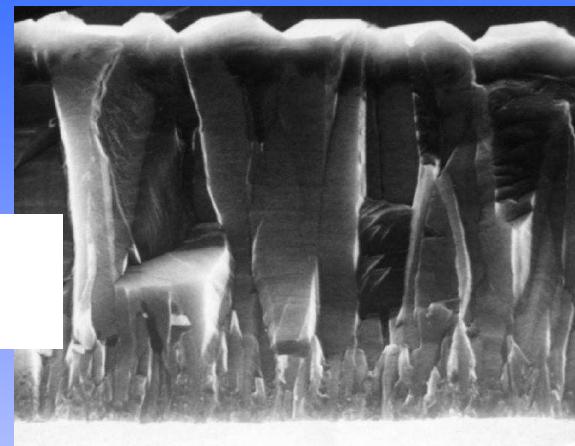
COMPARISON: DIAMOND ON Si ⇌ DIAMOND ON Ir/SrTiO₃

The film surface

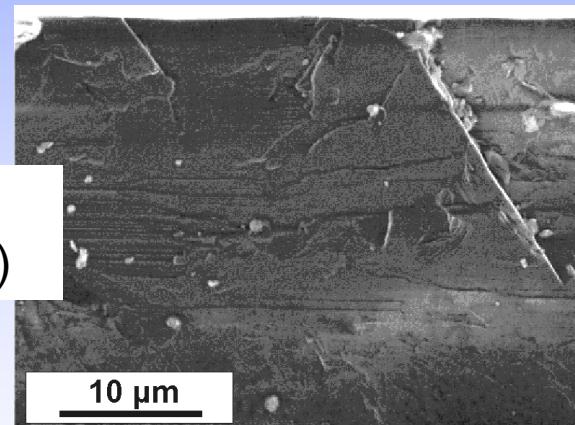


Diamond on
silicon

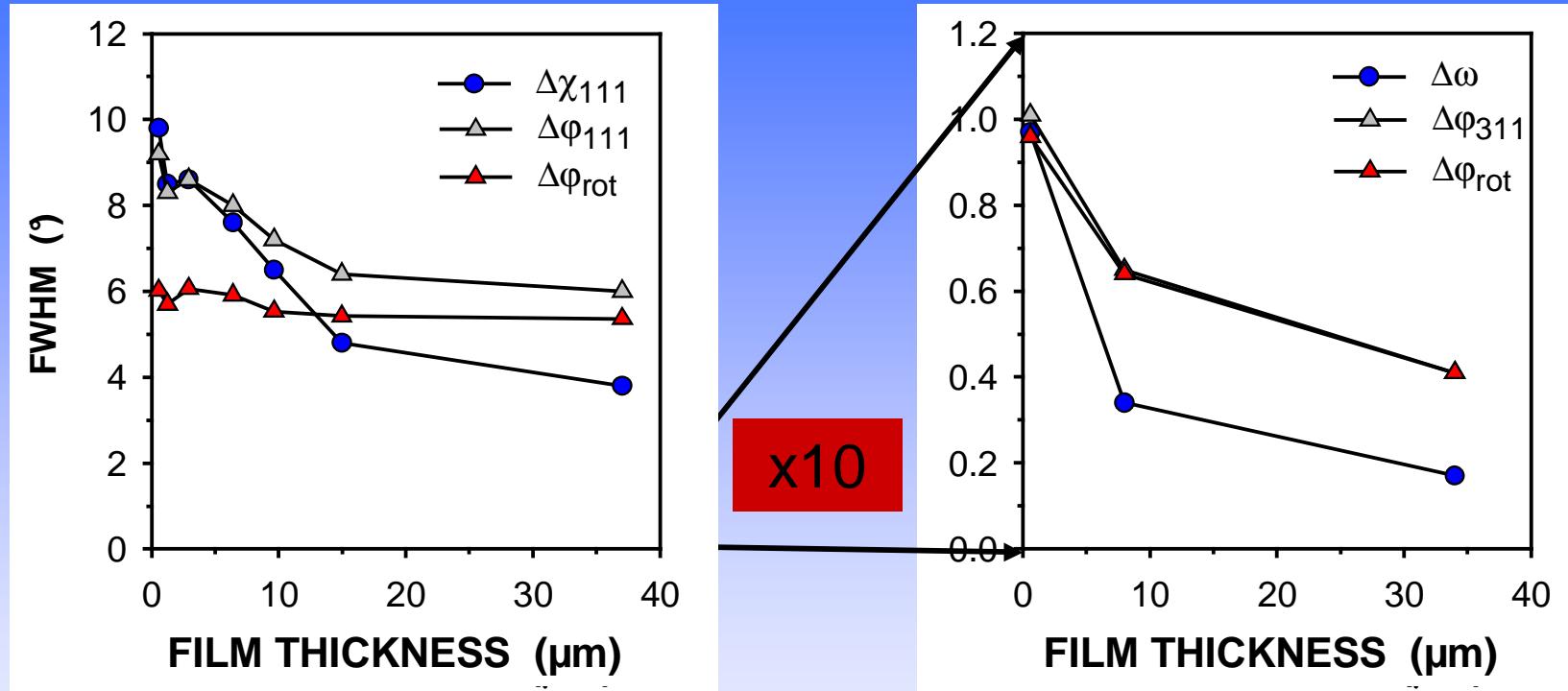
The cross section



Diamond on
Ir/SrTiO₃(001)



DIFFERENCES IN THE TEXTURE DEVELOPMENT: DIAMOND ON Si \leftrightarrow DIAMOND ON Ir/SrTiO₃

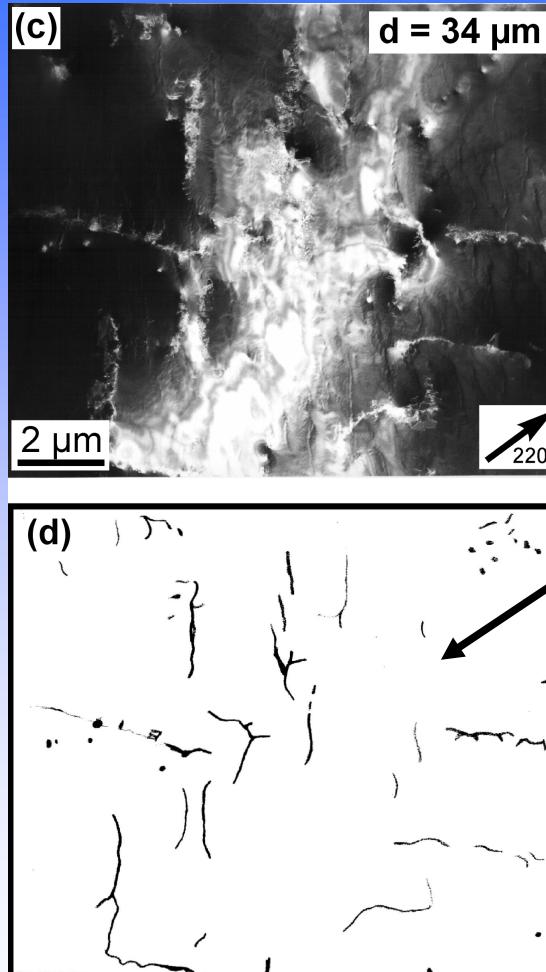
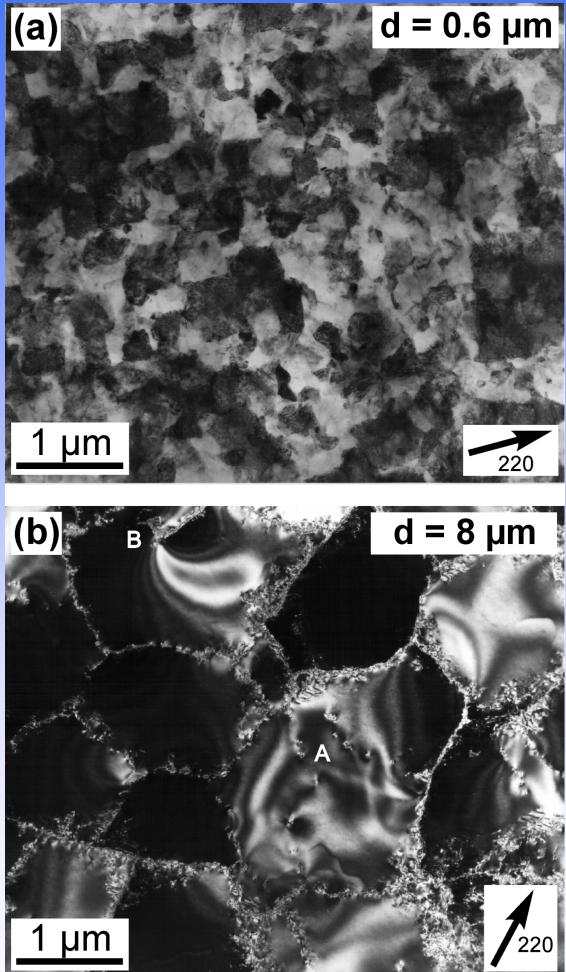


→ One order of magnitude lower mosaicity

→ Tilt and Twist decrease with thickness



INTERNAL DEFECT STRUCTURE: TRANSMISSION ELECTRON MICROSCOPY (TEM)



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

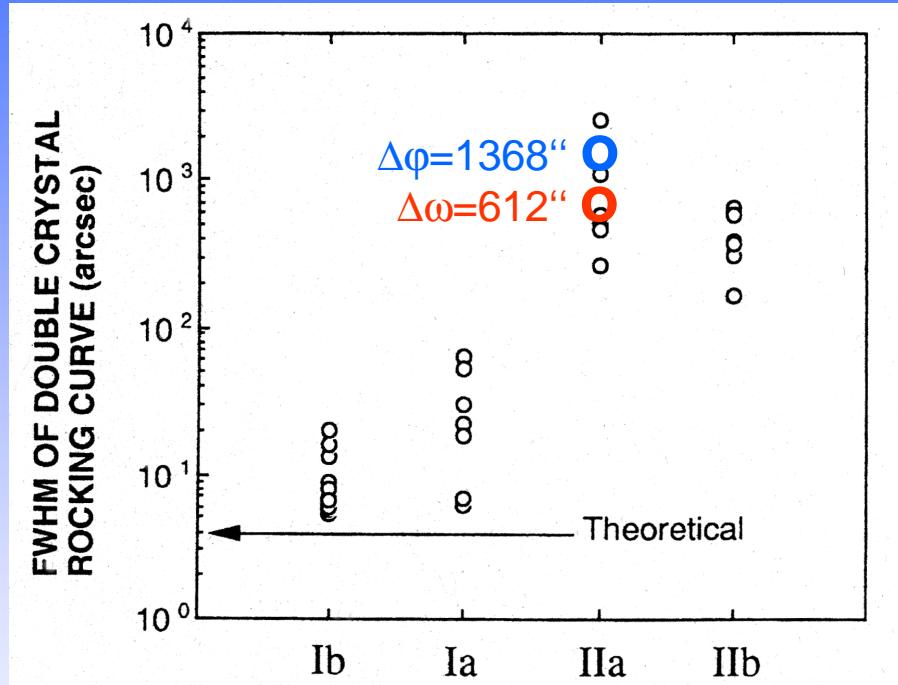
First single crystal diamond films by heteroepitaxy!

APL 78 (2001) 192



COMPARISON WITH NATURAL DIAMOND SINGLE CRYSTALS

Mosaicity



Typical rocking curve widths for different types of diamond crystals

Ref. S. Fujii et al. Appl. Phys. A 61 (1995) 331

Dislocation densities:

Our films: $5-10 \times 10^8 \text{ cm}^{-2}$

Large natural type IIa-diamonds:
typical $> 10^8 \text{ cm}^{-2}$
Ref.: A.R. Lang in *The Properties of Diamond* ed. by J. E. Field
(Academic, London 1979)



COMPARISON WITH COMPETING MATERIALS: GaN

TABLE 1 FWHMs of X-ray diffraction from GaN films. $\Delta\omega_c$, $\Delta\omega_a$ and $\Delta\omega$ show FWHMs of the ω -mode profile, while Δc and Δa show those of the $2\theta/\omega$ -mode profile.

	(0002)		(10-10)		(20-24)		d (μm)
	$\Delta\omega_c$	Δc	$\Delta\omega_a$ (arc sec)	Δa (arc sec)	$\Delta\omega$		
OMVPE GaN/sapphire	406	23	599	55	222	1.81	
OMVPE GaN/sapphire [9]	299						
MBE GaN/sapphire	48	33	5500	-	284	0.76	
OMVPE GaN/SiC	211	66	320	55	197	3.0	
<hr/>							
Diamond/Ir/SrTiO ₃	612		1368				
	tilt		twist				

Ref.: H. Amano and I. Akasaki: X-ray diffraction characterisation of GaN-based materials: triple axis diffractometry

In: Gallium Nitride and Related Semiconductors (emis Datareviews Series No. 23, 1999)



What is this material good for?

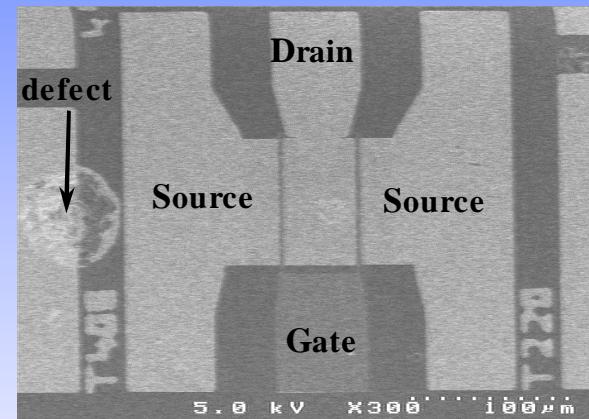
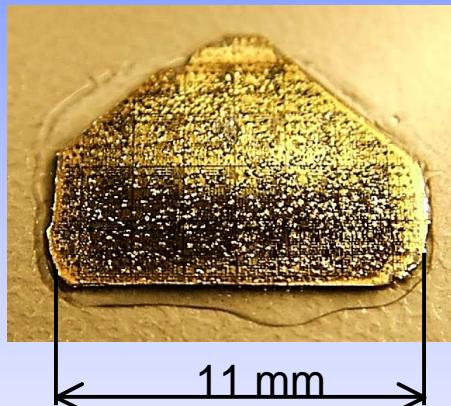


FIELD EFFECT TRANSISTORS REALISED ON Dia/Ir/SrTiO₃ SAMPLES

Device (FET) based on p-type surface conductive layer

Cooperation with Uni Ulm: M. Kubovic, A. Aleksov, M. Schreck, T. Bauer, B. Strizker, E. Kohn,
presented at Diamond 2002, Granada

The substrate



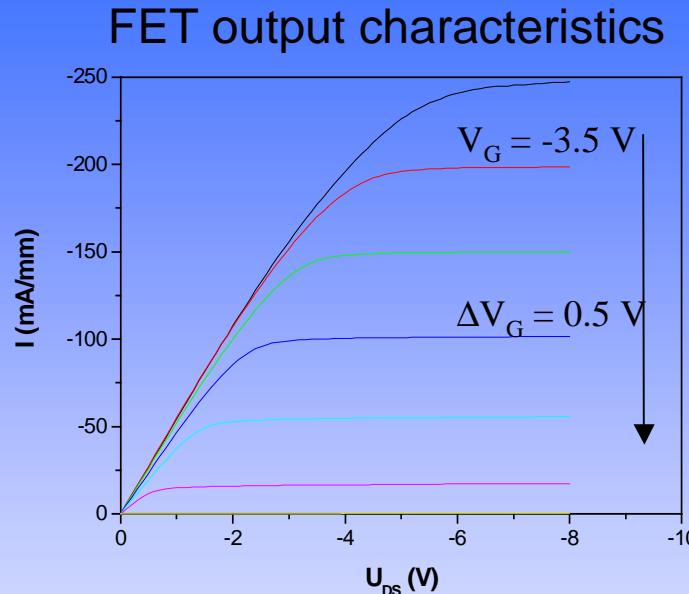
FET Device-Parameters

$$L_G = 0.2 \text{ } \mu\text{m}$$

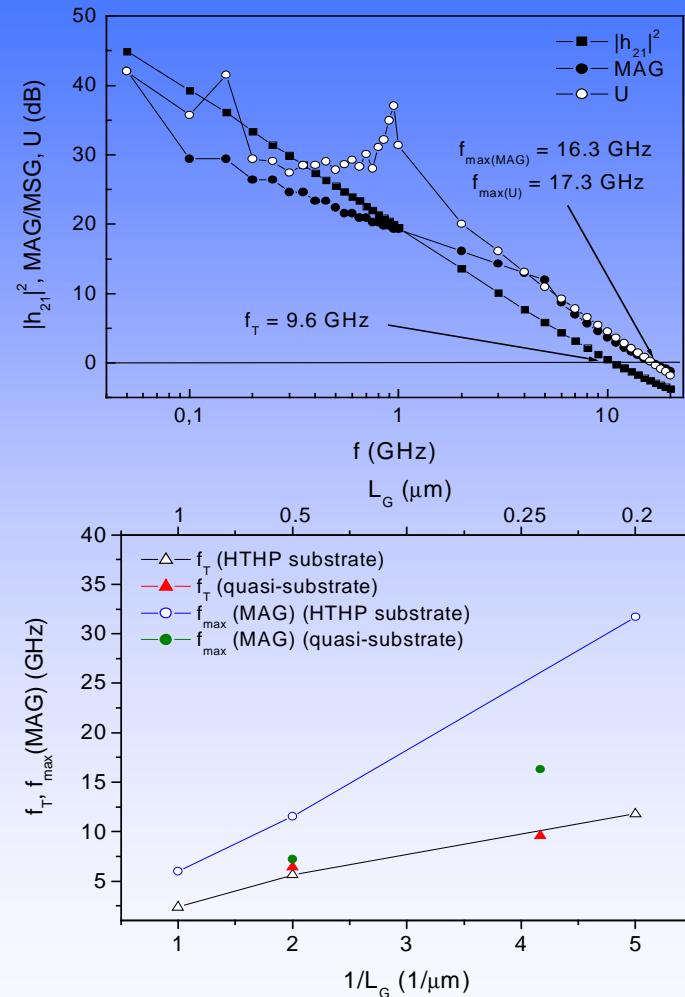
$$W_G = 100 \text{ } \mu\text{m}$$



FIELD EFFECT TRANSISTORS REALISED ON Dia/Ir/SrTiO₃(001) SAMPLES



Results: transconductance $g_{(mMAX)} = 97$ mS/mm
high break down field strength
Operation at microwave frequencies demonstrated
Properties approach values measured for homoepitaxial layers!!

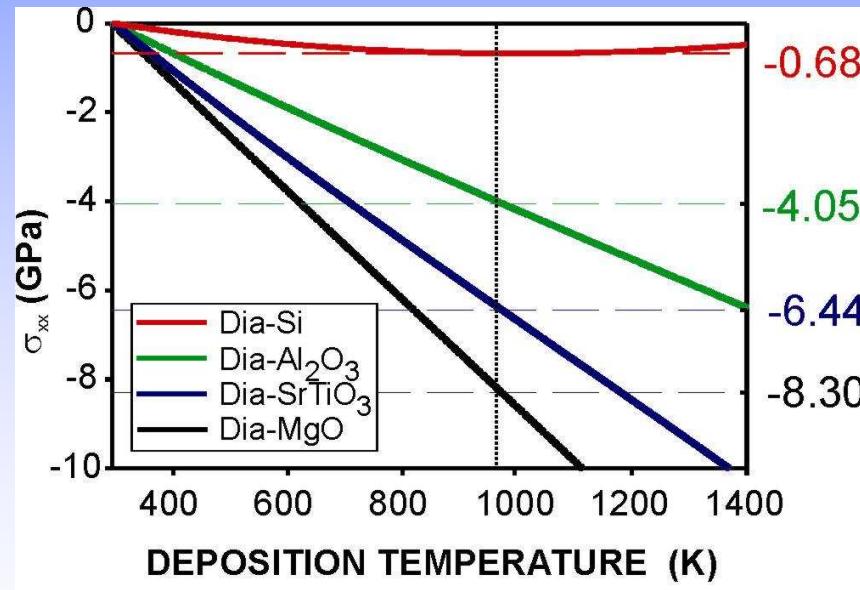


How to produce wafers from this material?



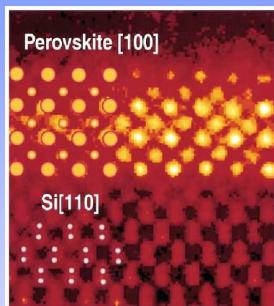
WHAT IS THE IDEAL SUBSTRATE FOR THE GROWTH OF LARGE AREA IRIDIUM FILMS AND THE GROWTH OF DIAMOND??

- Oxide crystals facilitate the deposition of single crystal metal layers
- Some are available in large size at affordable costs (e.g. sapphire)
- However: The fit of thermal expansion coefficients is poor



OXIDE BUFFER LAYERS ON SILICON AS HIGH-K DIELECTRICS & EPITAXIAL GROWTH SURFACE

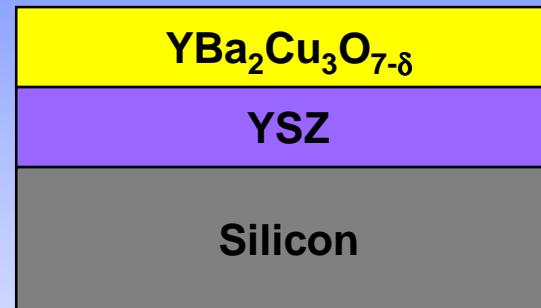
R. A. McKee, F. J. Walker, and M. F. Chisholm: *Crystalline Oxides on Silicon: The First Five Monolayers*, Phys. Rev. Lett. 81 (1998) 3014.



Deposition method:

Molecular beam epitaxy (MBE)

A. Bardal, M. Zwerger, O. Eibl, J. Wecker, Th. Mathee, *YBa₂Cu₃O_{7-δ} films on Si with Y-stabilized ZrO₂ and Y₂O₃ buffer layers: High resolution electron microscopy of the interfaces* Appl. Phys. Lett. 61 (1992) 1243.



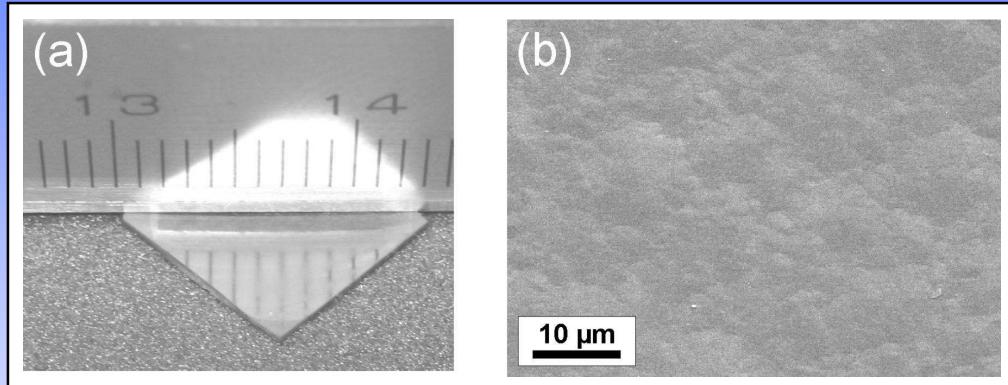
Deposition method:

Pulsed laser deposition (PLD)

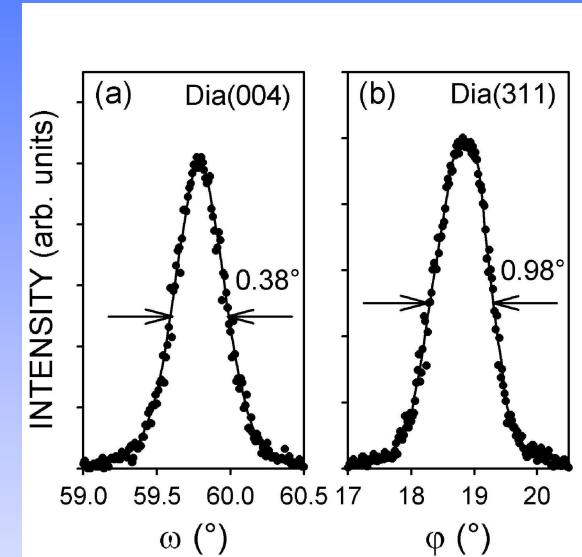


ALTERNATIVE 1: EPITAXIAL DIAMOND FILM ON Ir/SrTiO₃/Si(001) (THICKNESS: 16 μm)

Surface



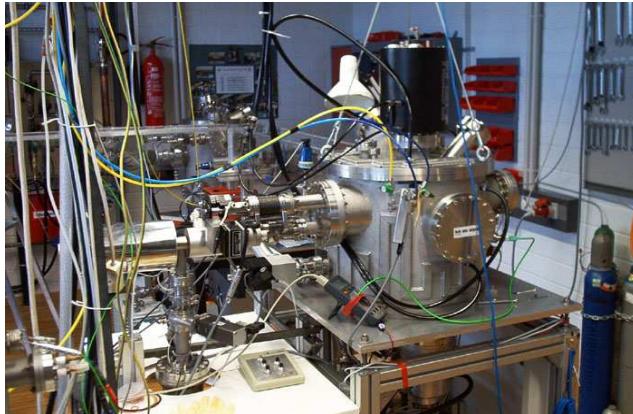
Texture



ALTERNATIVE 2: YSZ ON Si PREPARED BY PLD

Pulsed laser deposition (PLD) setup

Laser pulse



KrF excimer laser

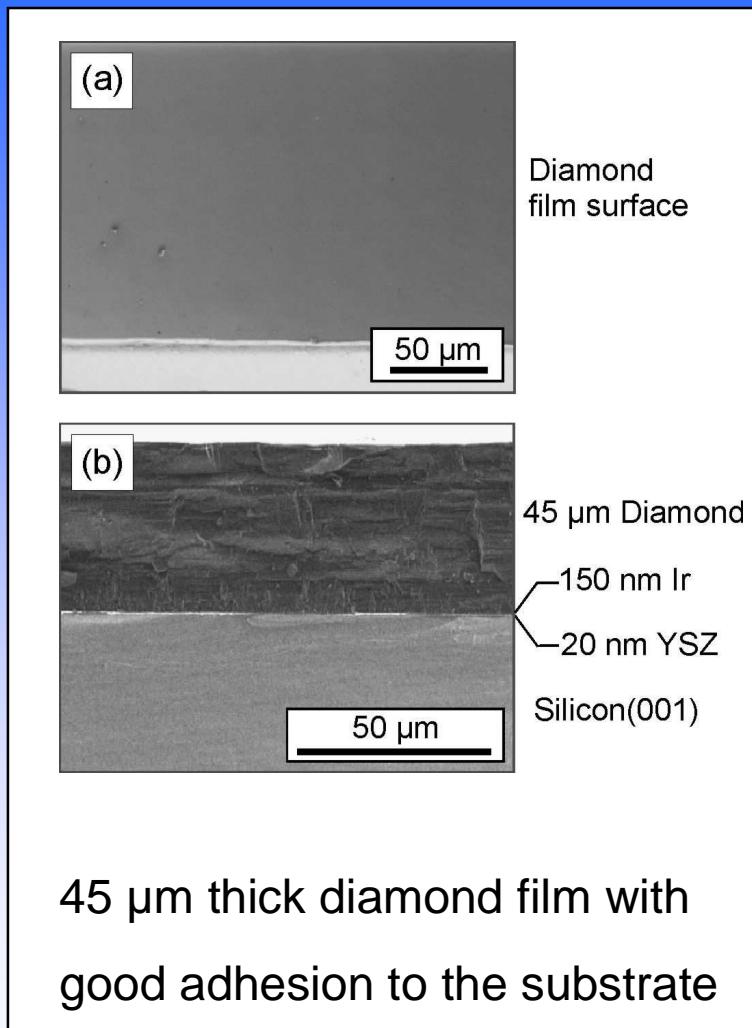
25 ns pulses of 850 mJ

Yttria stabilized zirconia (YSZ) film deposition:

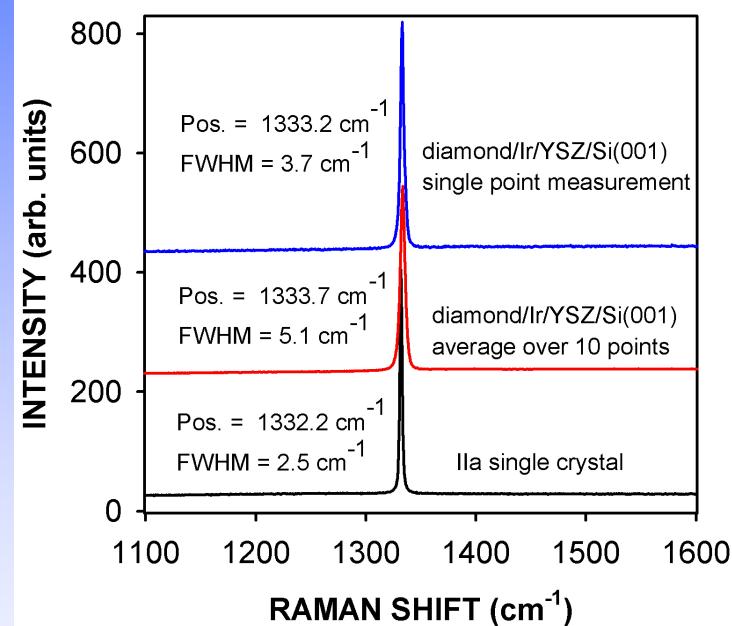
- no removal of the silicon oxide
- ablation target: (ZrO_2) stabilized with Y_2O_3
- 5×10^{-2} Pa oxygen (First 600 pulses without oxygen)
- substrate temperature: 825°C
- thickness: 20 nm (40 nm)



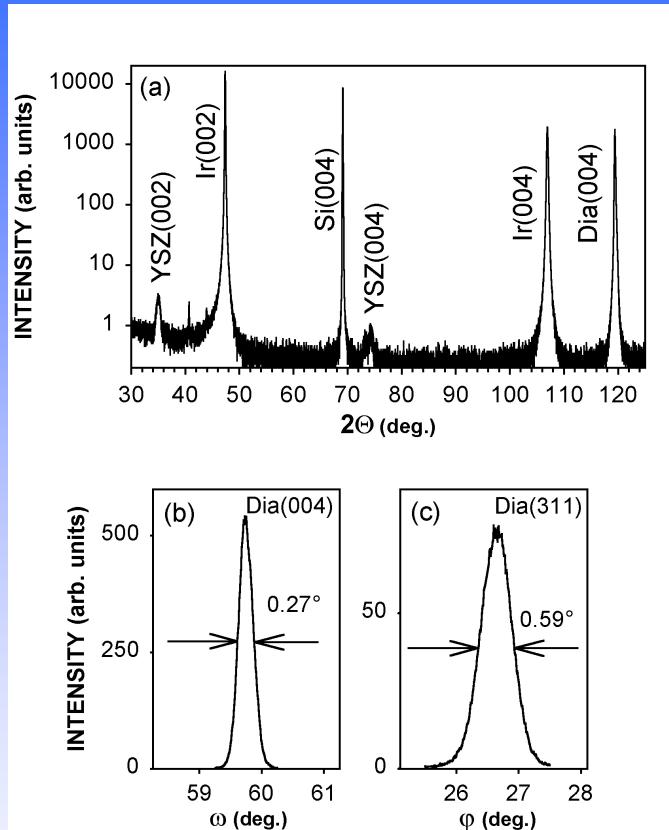
THICK DIAMOND FILMS ON Ir/YSZ/Si(001)



μ-Raman measurements



THICK DIAMOND FILMS ON Ir/YSZ/Si(001): THE TEXTURE



For comparison: Dia/Ir/SrTiO₃(001)

0.17° (Tilt) and 0.38° (Twist)

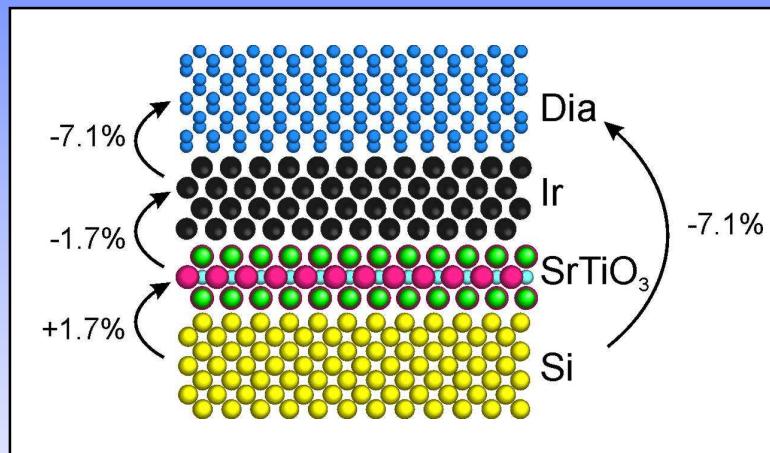
S. Gsell et al., Appl. Phys. Lett. 84
(2004) 4541.



HOW IS THE HUGE LATTICE MISFIT ACCOMMODATED IN THE TWO CASES?

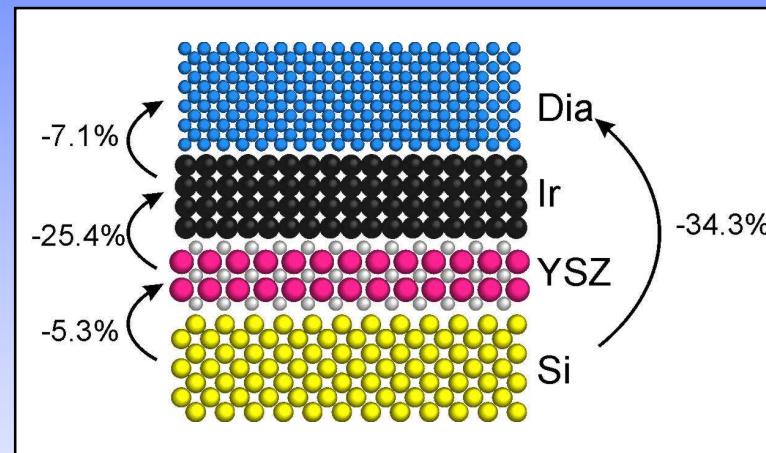
1) Dia/Ir/SrTiO₃/Si(001)

(45° rotation of SrTiO₃ vs. Si)



2) Dia/Ir/YSZ/Si(001)

(cube on cube)



Current status:

4 inch wafers of Ir/YSZ/Si(001) have been realized



SUMMARY

- ◆ Iridium, an extraordinary material for the nucleation of oriented diamond
- ◆ silicon the **old and new favorite** as supporting substrate for diamond heteroepitaxy
- ◆ 2 alternative buffer layers for the deposition of Ir on Si
- ◆ reasonable good epitaxy and adhesion of the diamond films in both cases
- ◆ technical issues (preparation, scalability, ultimate quality) may determine which concept will make the race!

