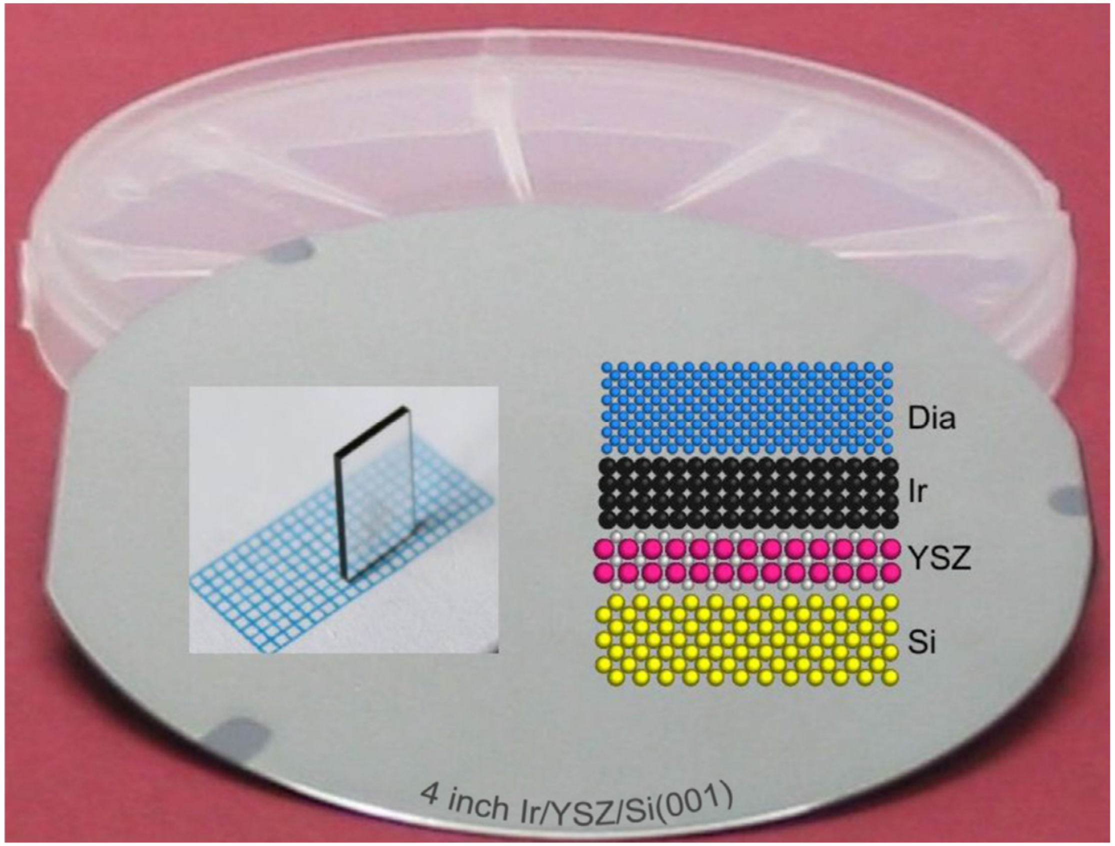
Recent progress in the growth of heteroepitaxial diamond for detector applications

4th ADAMAS Workshop at GSI

2015-12-03 – 2015-12-04

Michael Mayr, Oliver Klein, Martin Fischer,
Stefan Gsell, Matthias Schreck

Heteroepitaxial diamond growth



Substrate for diamond growth:
4 inch Ir/YSZ/Si(001) wafer

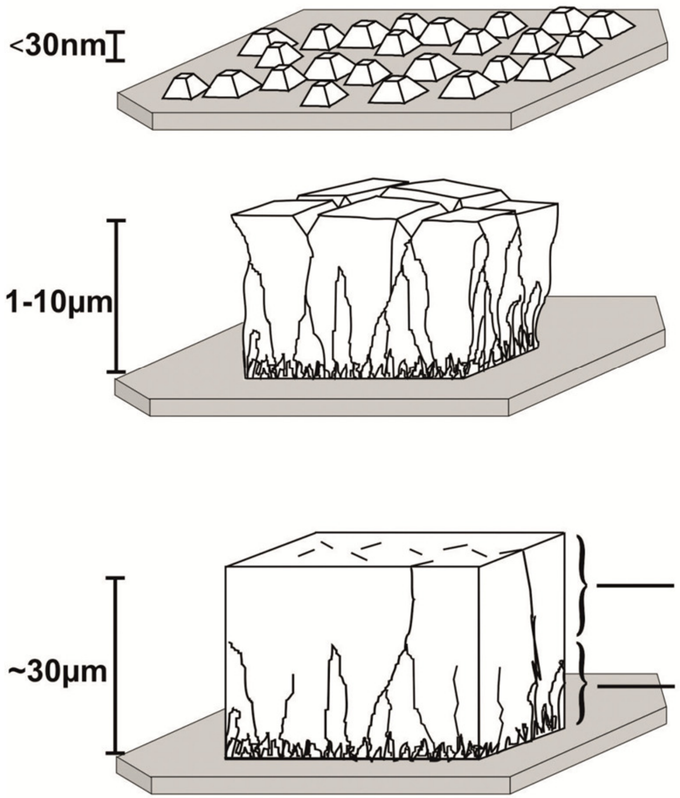
Multi-layer-system **(Ir/YSZ/Si(001))**
YSZ: yttria (Y_2O_3) - stabilized zirconia (ZrO_2)

BEN (bias enhanced nucleation) step on Iridium
→ formation of epitaxial diamond nuclei

Off-axis growth:
→ beneficial for suppression of non-epitaxial grains

2 off-axis directions:
(001) off-axis towards [100]
(001) off-axis towards [110]
realized by miscut of Si-substrate

Variation of the defect structure with film thickness



Phase 1:
isolated diamond crystallites on iridium layer

Phase 2:
highly oriented diamond layer: individual mosaic blocks separated by small angle grain boundaries

Phase 3: transition to single crystal layer
single crystal region with isolated and clustered dislocations
mosaic block region

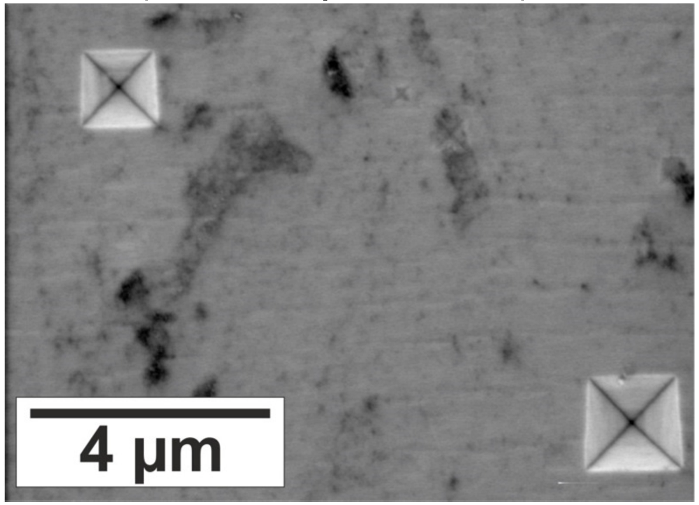
Major remaining defects:
+ single dislocations
+ clusters of dislocations

How can one derive the quality of the film, specifically the density of dislocations?

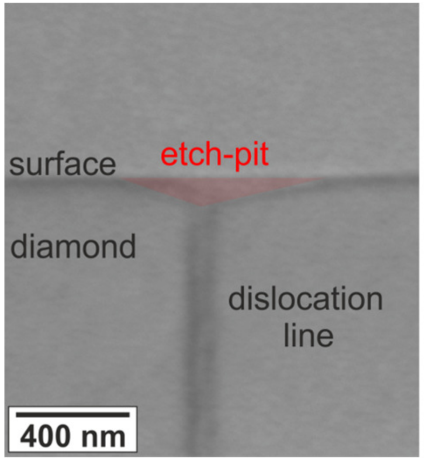
Etch-pit technique for visualization and quantification of threading dislocations

Preferential etching in H_2/CO_2 – Plasma → creation of **etch-pits**

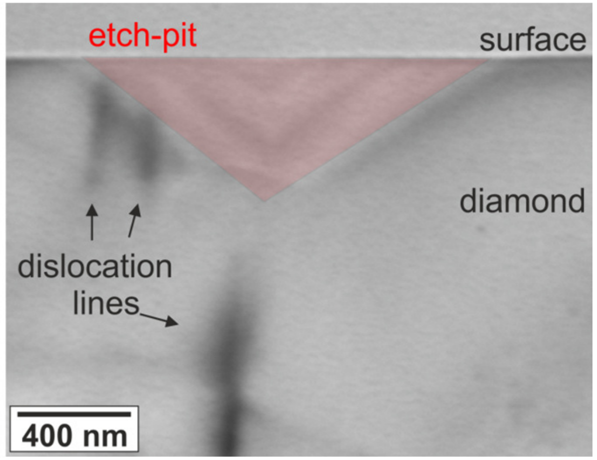
SEM (surface plan view):



TEM (cross-section):

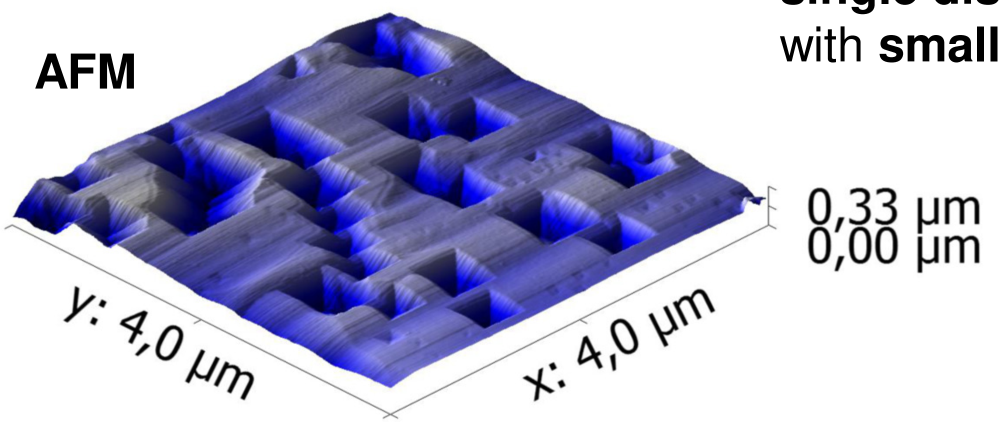


single dislocation with **small** etch-pit



occasionally several neighbouring dislocations lead to **one large** etch-pit

AFM



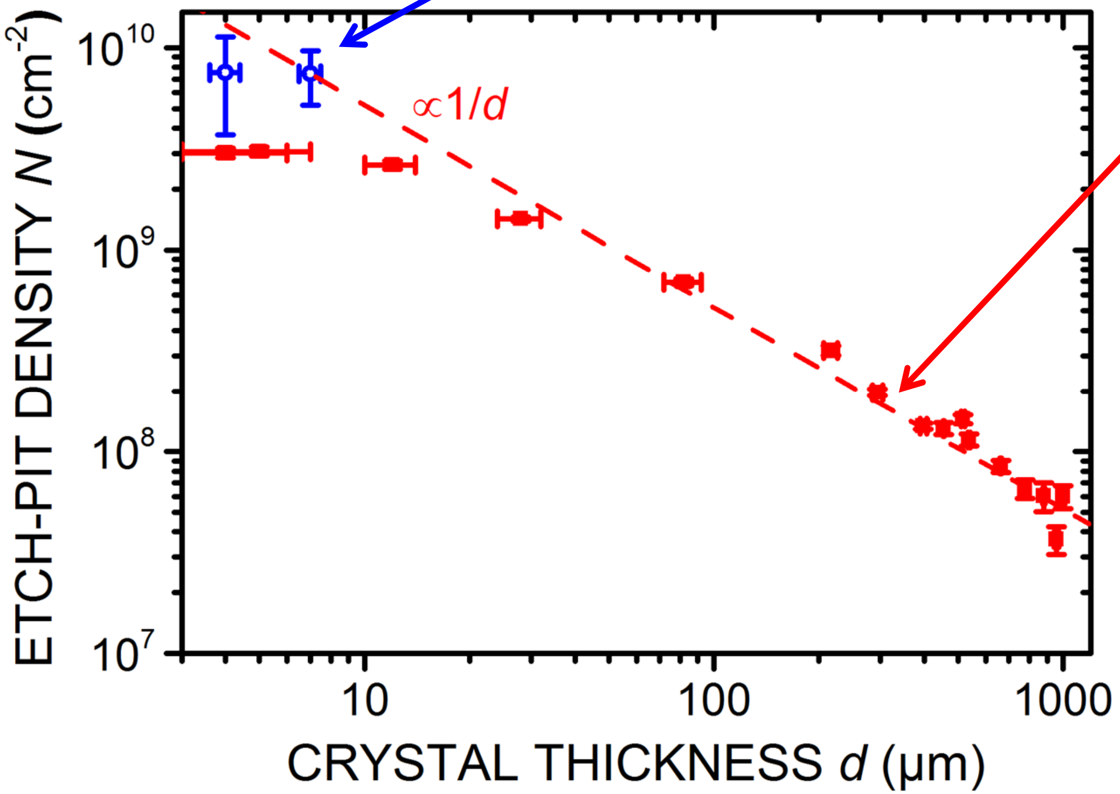
→ counting of etch-pits leads to the etch-pit density

→ good estimation of dislocation density

Variation of etch-pit density with crystal thickness

shown earlier:

Data points from TEM measurements



Data points from etching experiments

Extended growth of **1000 µm** of diamond:

➔ dislocation density drops from **>10^{10}** to **<10^{8}** cm^{-2}

C. Stehl et al. Appl. Phys. Lett. **103**, 151905 (2013)

Reactions between threading dislocations

Reactions between dislocations “i” and “j” forming a new dislocation “k”:

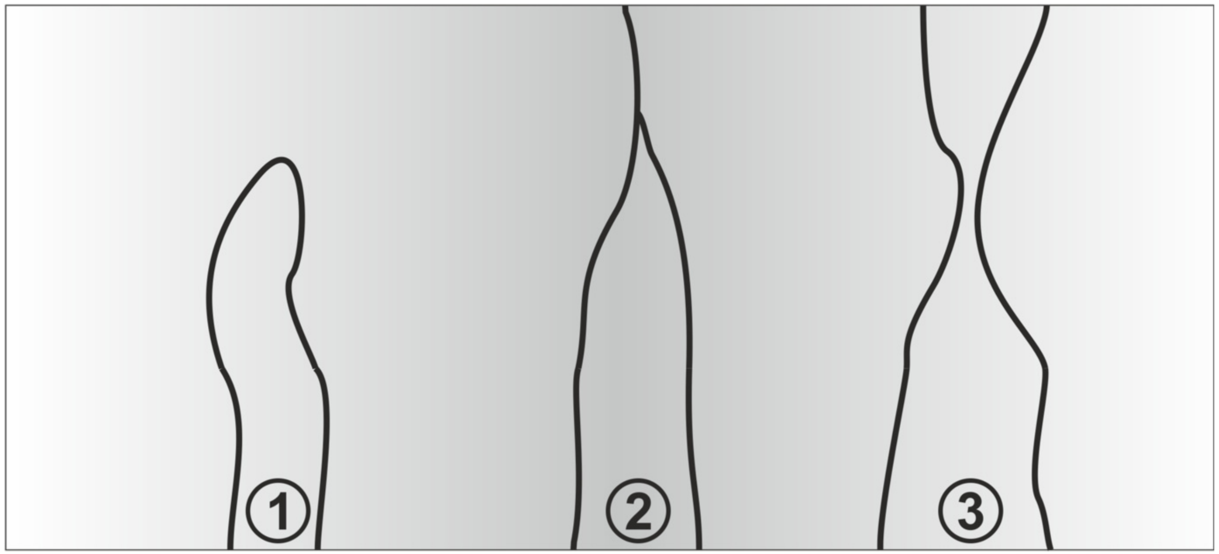
$$\mathbf{b}_k = \mathbf{b}_i + \mathbf{b}_j \quad \textit{(sum of the Burgers vectors)}$$

According to Frank´s energy criterion:

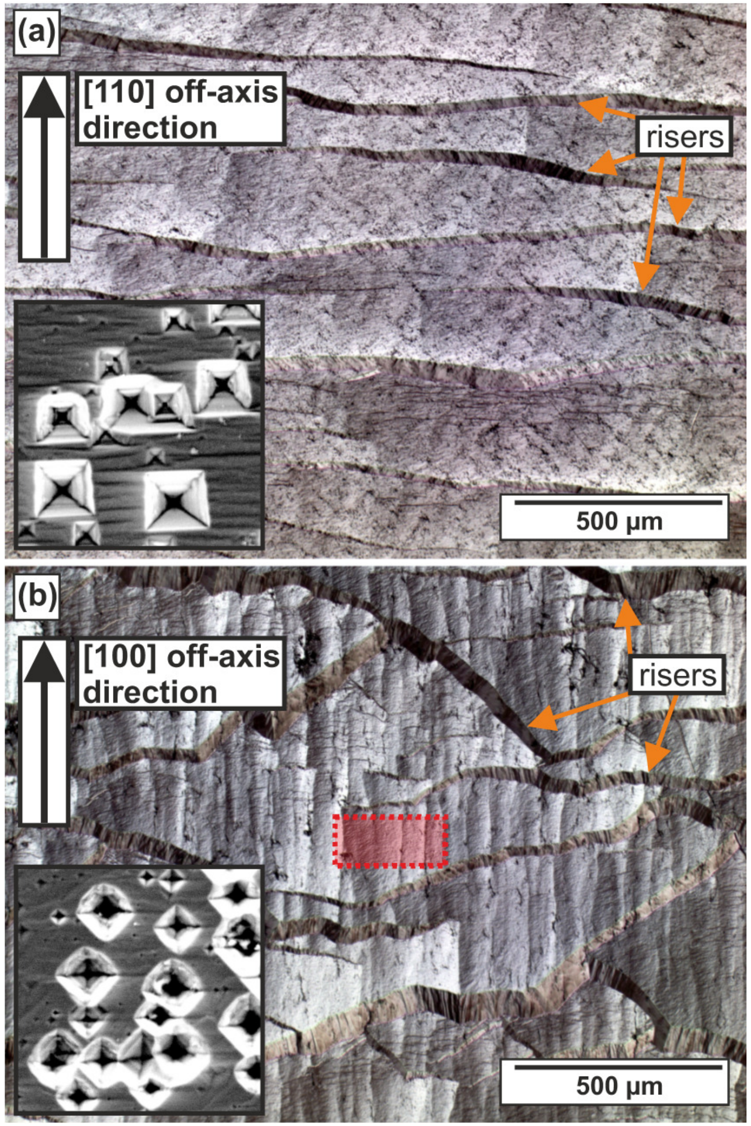
(1) $b_k = 0$ Annihilation: i + j ➔ both dislocations stop (“half-loop”)

(2) $b_k^2 \leq b_i^2 + b_j^2$ Fusion: i + j ➔ k (“y-shape”)

(3) $b_k^2 > b_i^2 + b_j^2$ Scattering i + j ➔ i + j (both dislocations proceed in layer)



Inhomogeneous distribution of etch pits depending on off-axis direction



DIC optical micrographs of diamond grown (30 ppm N_2) on Ir/YSZ/Si(001) using Si(001) substrates with 4° off-axis angle toward

(a) [110]

(b) [100]

after plasma-etching for visualization of dislocations.

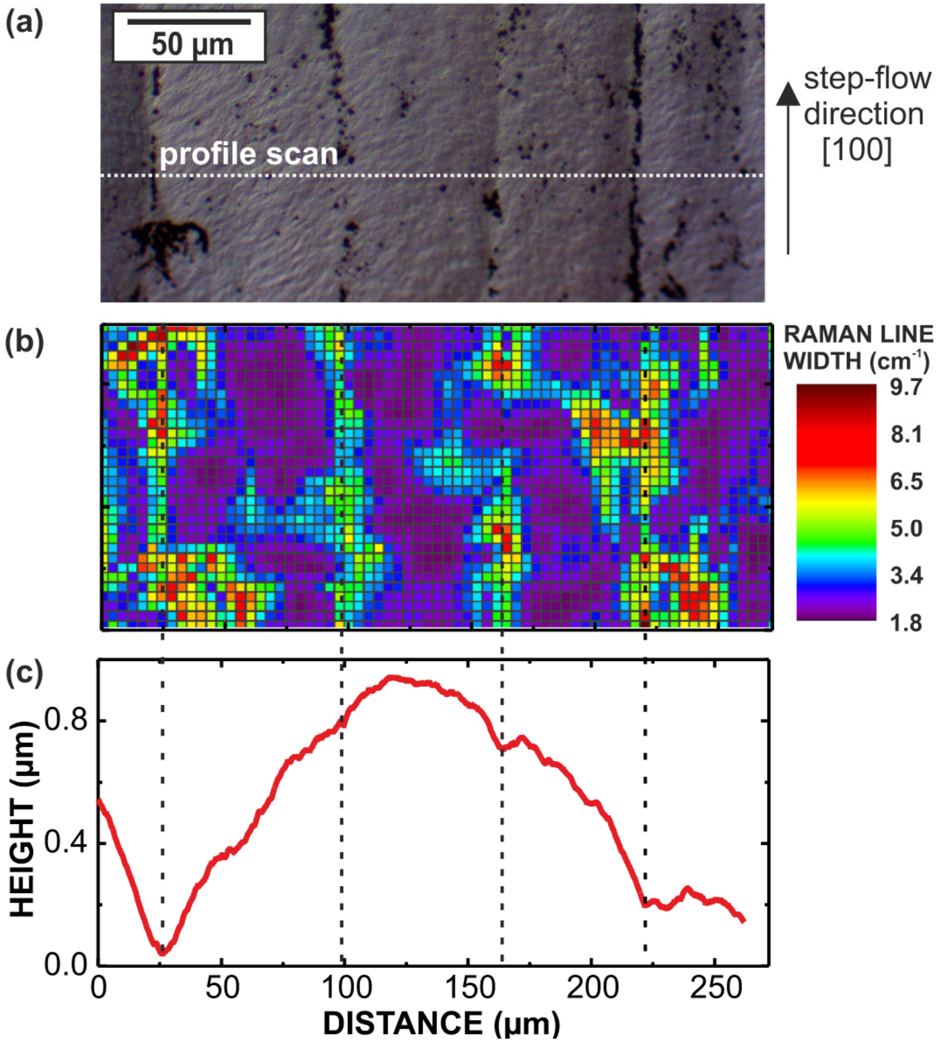
Dark spots arranged in bands are due to etch pits

Different etch-pit patterns:

(a) cross – pattern

(b) straight lines along one axis

Etch-pit distribution and Raman-mapping of etch-pits on as-grown (001) [100] off-axis surface



Preferential etching of dislocations on a non-polished („as-grown") (001) off-axis towards [100] surface:

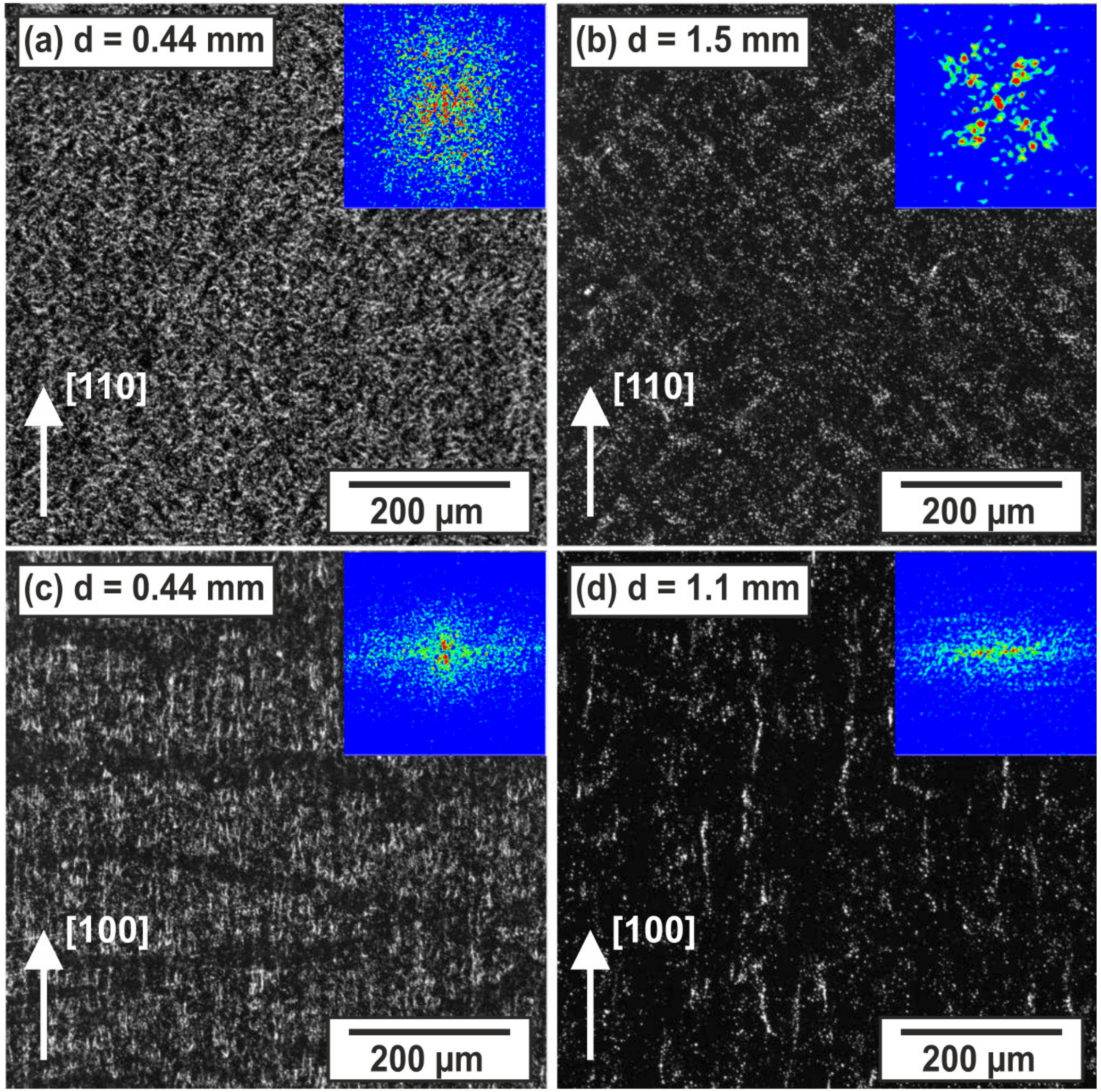
→ aggregation of dislocations in lines along the off-axis direction

→ good agreement with Raman line-width measurements

→ etch-pits are predominantly agglomerated in shallow grooves

mechanism for this spatial redistribution of the defect?

Diamond etch pit patterns: FFT analysis



Polishing and further microwave plasma etch step
→ no more artefacts from topographic features

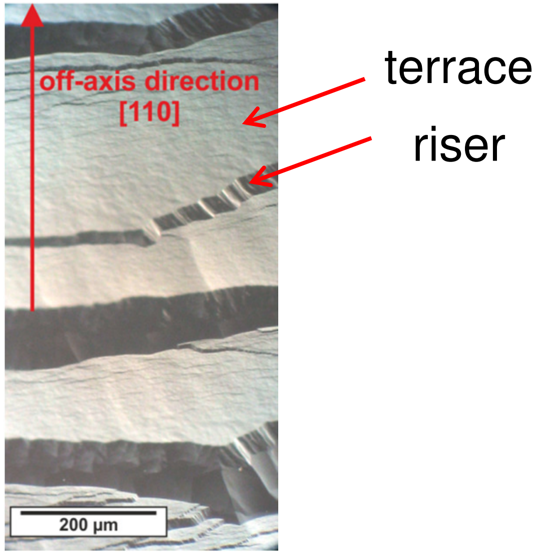
Laser slicing, polishing and etching to visualize distribution at intermediate stage of film growth
→ DF optical micrographs
→ FFT processing

Patterns not fully developed at 0.44 mm

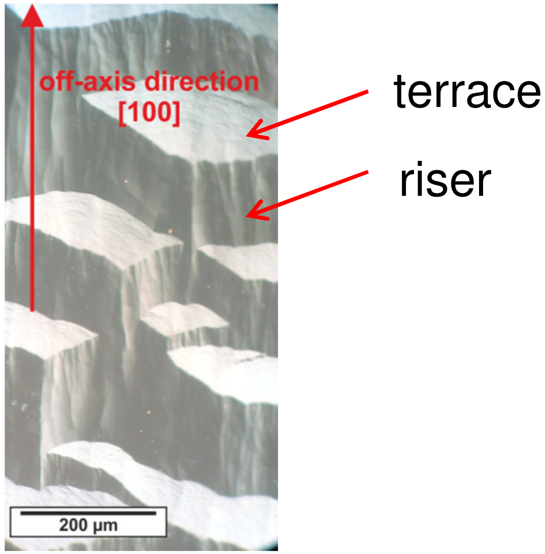
Confirmed:
(a),(b) cross – pattern
(c),(d) straight lines along one axis

Schematics of surface morphology for [110] and [100] off-axis direction

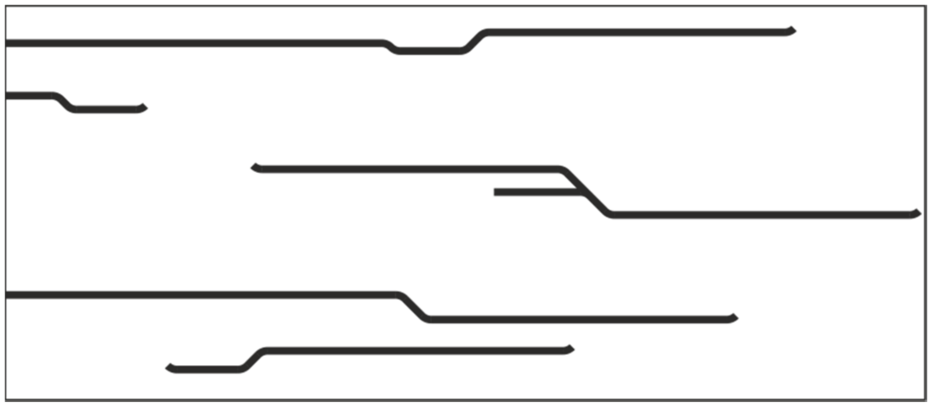
Can morphological features offer the key to the understanding of the phenomena?

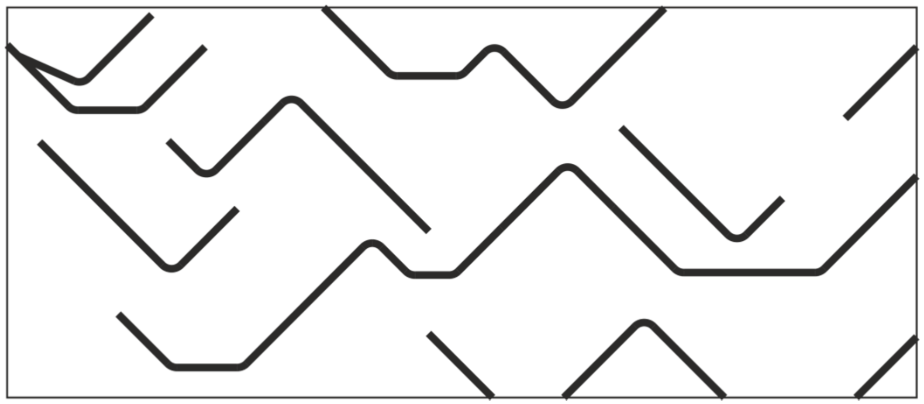


straight lines



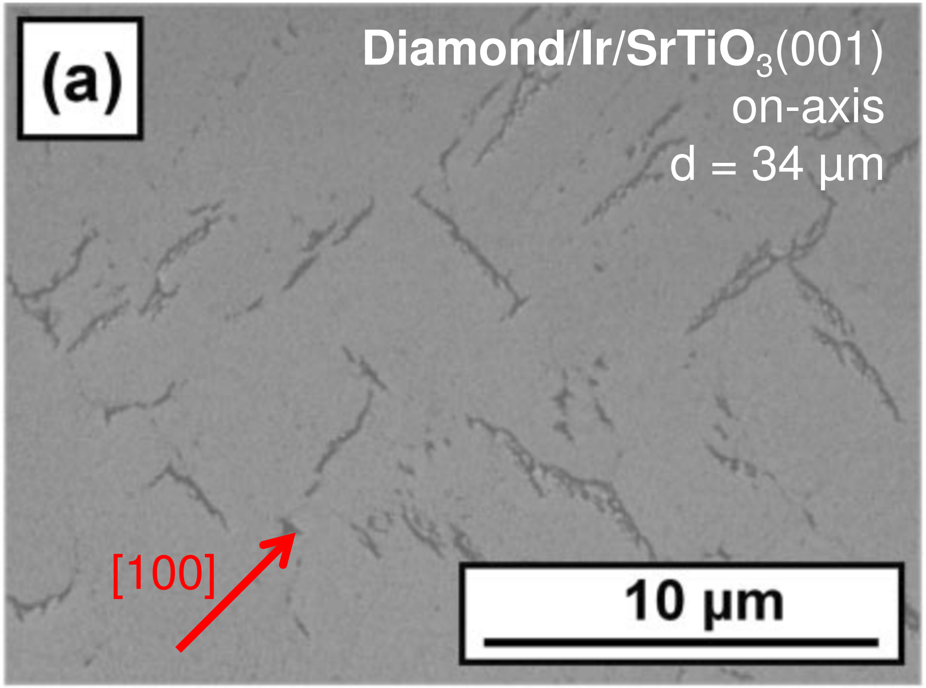
zig-zag structure





Driving forces for preferential alignment of dislocations along <100>

For [110] off-axis:
preferntial alignment of dislocation clusters neither parallel, nor perpendicular to off-axis direction!
BUT along [100] direction. **Why?**



M. Schreck et al., J. Appl. Phys. 91, 676 (2002)

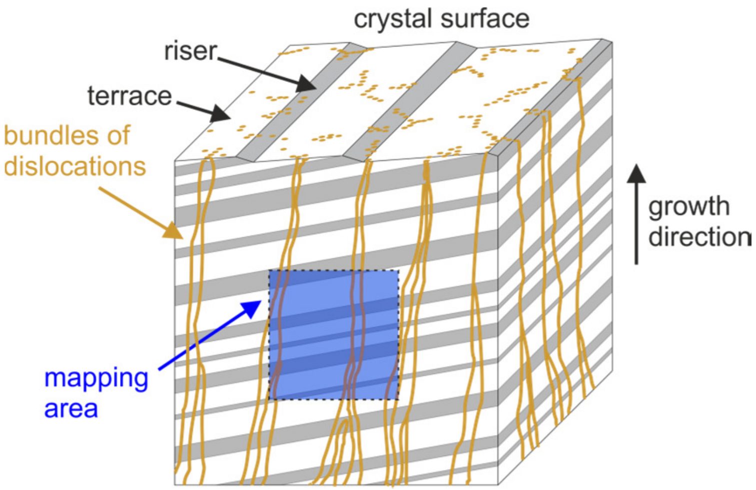
Grooves correlated with dislocation bands aligned along [100] and [010] directions

explanation:
crystallographic anisotropies in mutual interaction between neighbouring dislocations

Symmetry of patterns formed during [110] off-axis growth apparently not controlled by lateral step flow.

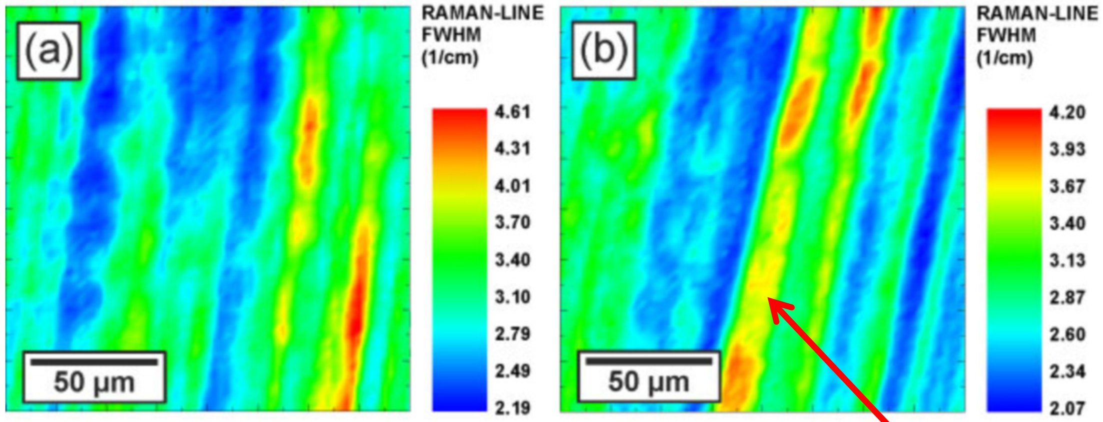
Preferential dislocation tilting in off-axis diamond growth as deduced from Raman maps

Lateral movement of dislocations requires a process that causes a controlled tilt of dislocations !



M. Mayr et al. phys. stat. sol. (a) 211, 10 (2014)

Maps of diamond Raman line width



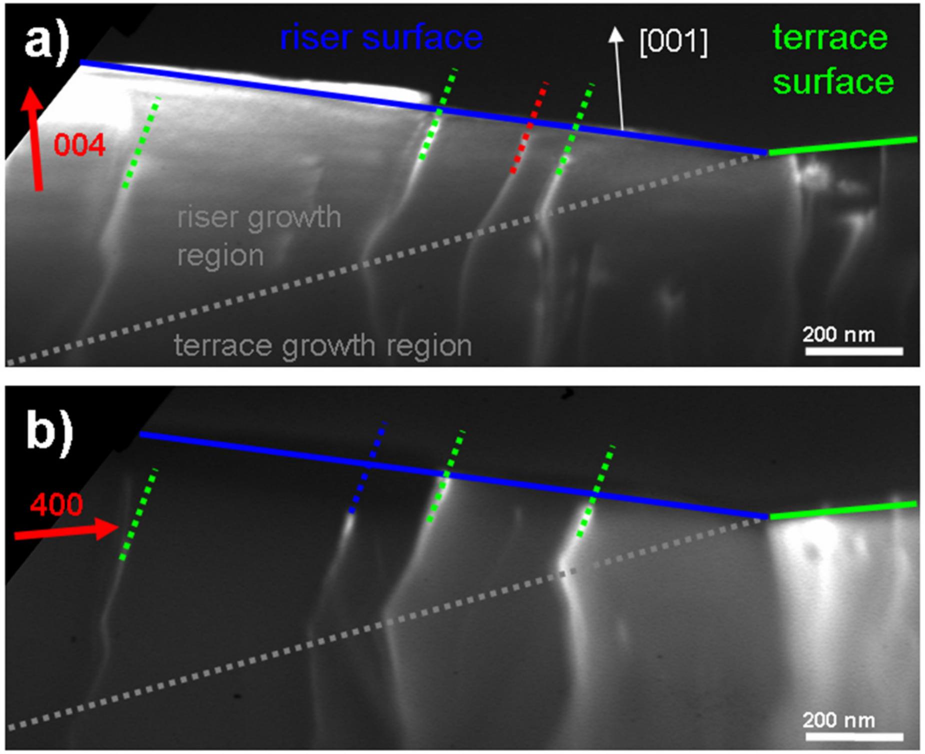
(a) [110] off-axis (b) [100] off-axis

Dislocation bundle!?

Maps of Raman line-broadening
→ lateral step flow induces tilt of propagating dislocation bundles!

➔ TEM for confirmation of tilt of individual dislocations

Diamond sample grown with 100 ppm nitrogen

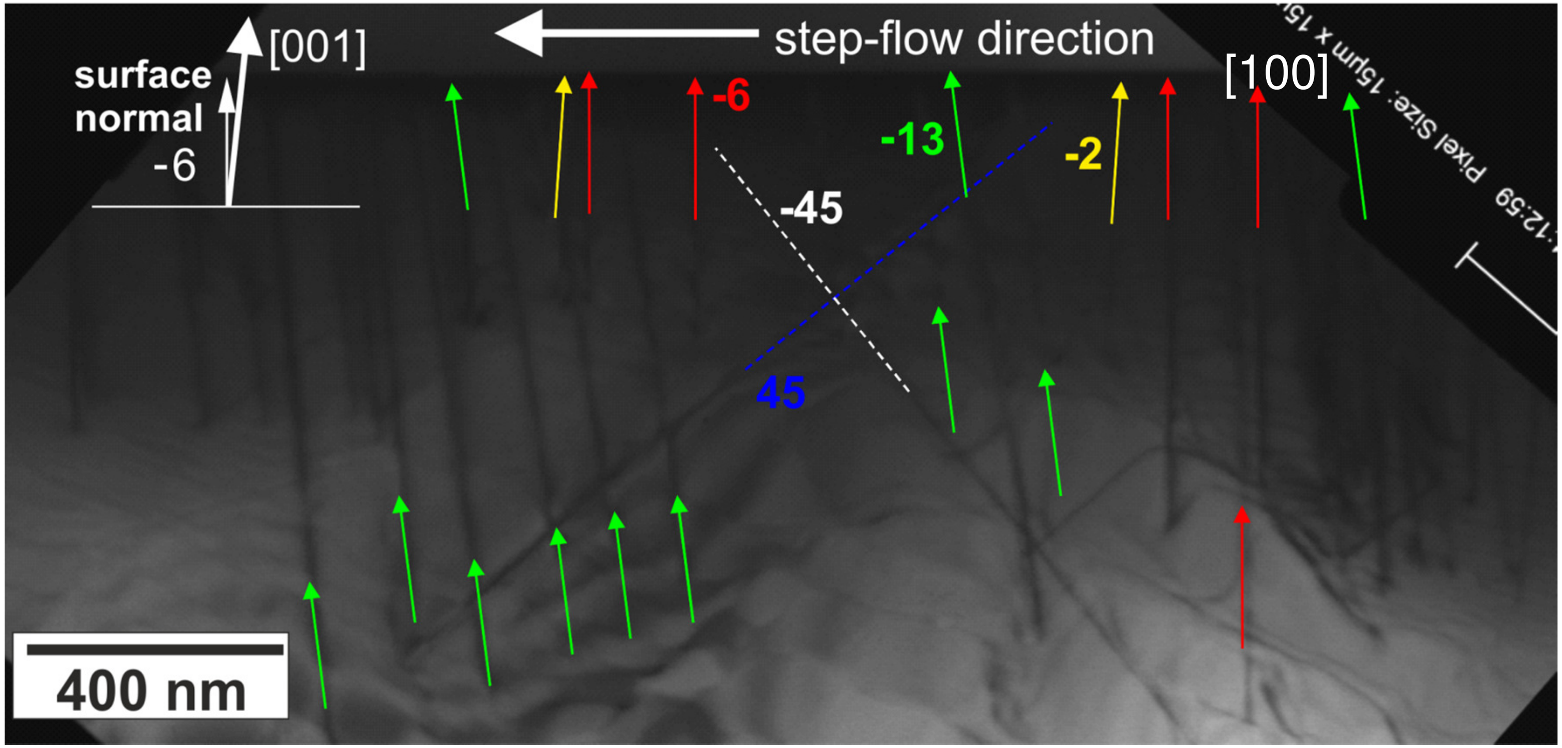


green:
45° dislocations with b = ½ [±10±1]
red:
45° dislocation with b = ½ [0±1±1]
blue:
90° dislocation with b = ½ [±1±10]

1. All dislocations are tilted in step-flow direction away from [001]
2. Switching of the angle occurs at the transition from riser to terrace area growth
3. Tilt angle is independent of Burgers vector

TEM cross-section

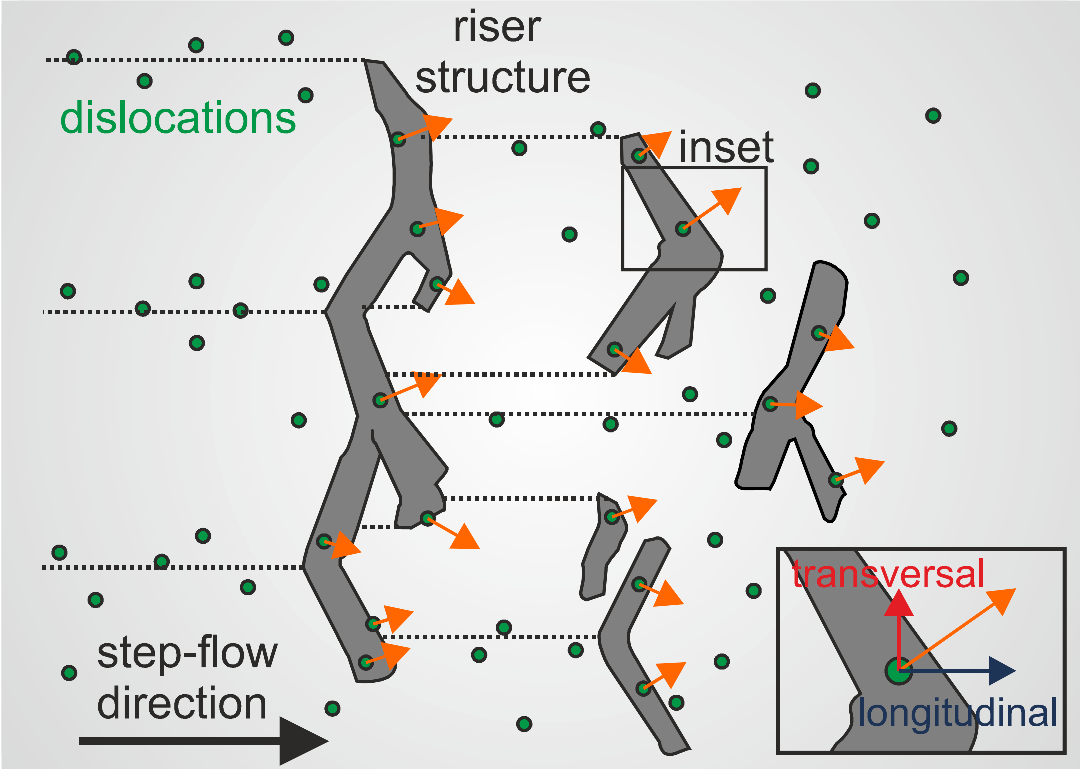
Diamond sample grown without nitrogen



1. All dislocations are tilted in step-flow direction away from [001]
2. 3 different groups of discrete tilt angles
3. Burgers vector analysis:

high tilt angles ⇔ **effective glide**
small tilt ⇔ **effective climb**

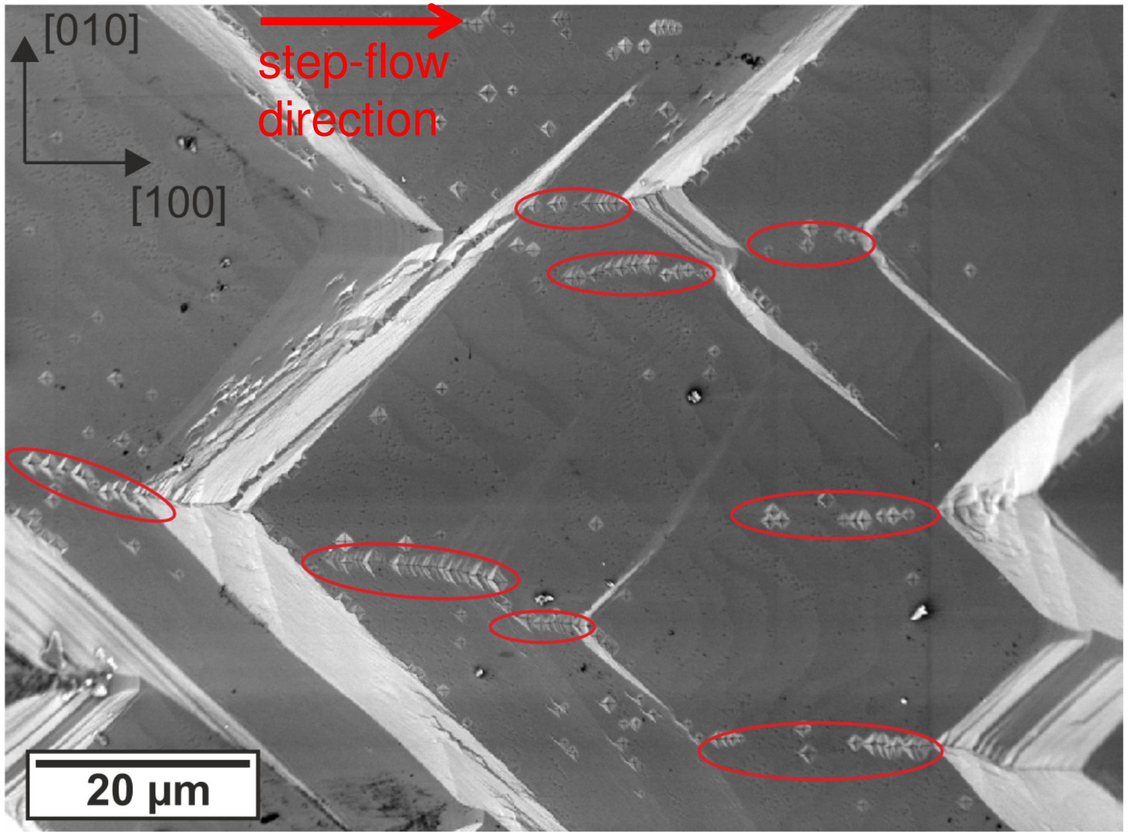
Model for spacial redistribution of dislocations by lateral step flow



Is it possible to observe this effect on single dislocations?

➔ Homoepitaxial growth experiments on HPHT substrates
(typical dislocation densities $10^4 – 10^6$ cm^{-2})

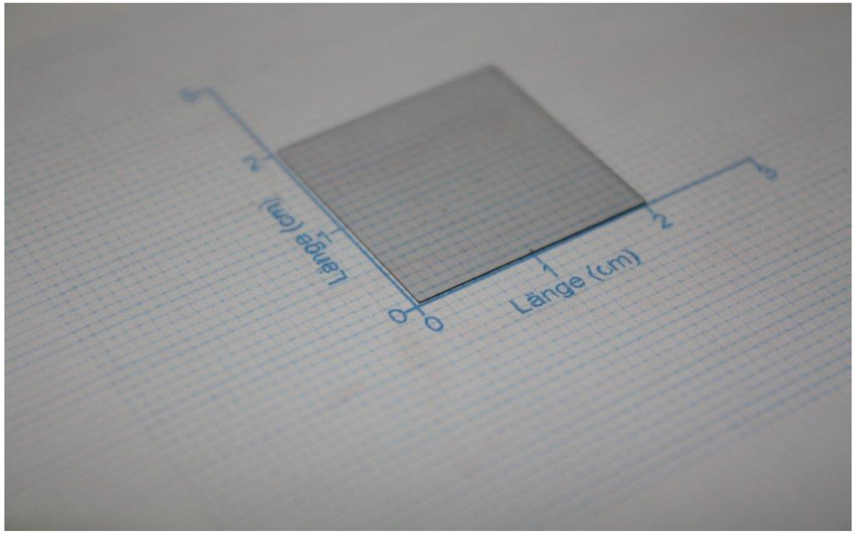
Collection and bundling of dislocations during growth



Preferential etching of dislocations and examination with SEM
→ Red ellipses highlight chains of etch-pits
→ Collection of dislocations and bundling during step-flow growth

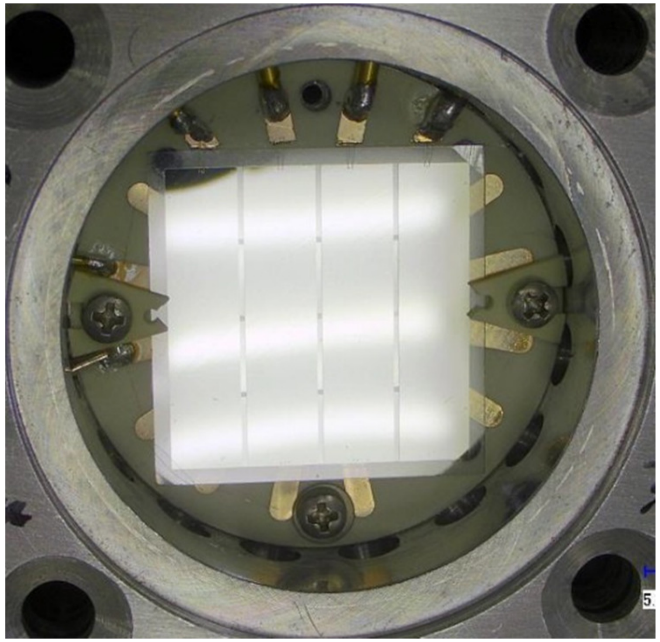
Recent progress in sample size

sample with lateral dimensions 2 x 2 cm^2:



Metallized and contacted for characterization

M. Kiš,
DIAMOND 2015, Bad Homburg, Germany



Summary

- Reduction of dislocation density with film thickness is associated with inhomogeneous spatial distribution
- Growth on (001) vicinal surfaces result in completely different patterns for [100] and [110] off-axis directions
- Square shaped pattern for (001)[110] off-axis are attributed to crystallographic bulk properties of diamond
- Stripe pattern on (001)[100] off-axis indicate a spatial redistribution of dislocations caused by lateral step flow
- Preferential tilting consistently observed in TEM and Raman maps

Results have been published:
Michael Mayr, Martin Fischer, Oliver Klein, Stefan Gsell and Matthias Schreck
Phys. Status Solidi A 212, No. 11, 2480– 2486 (2015) /
DOI 10.1002/pssa.201532243

Thank you for your attention!

Acknowledgements:

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