Unique properties of Pyrolytic Graphite for extreme conditions

Optigraph GmbH

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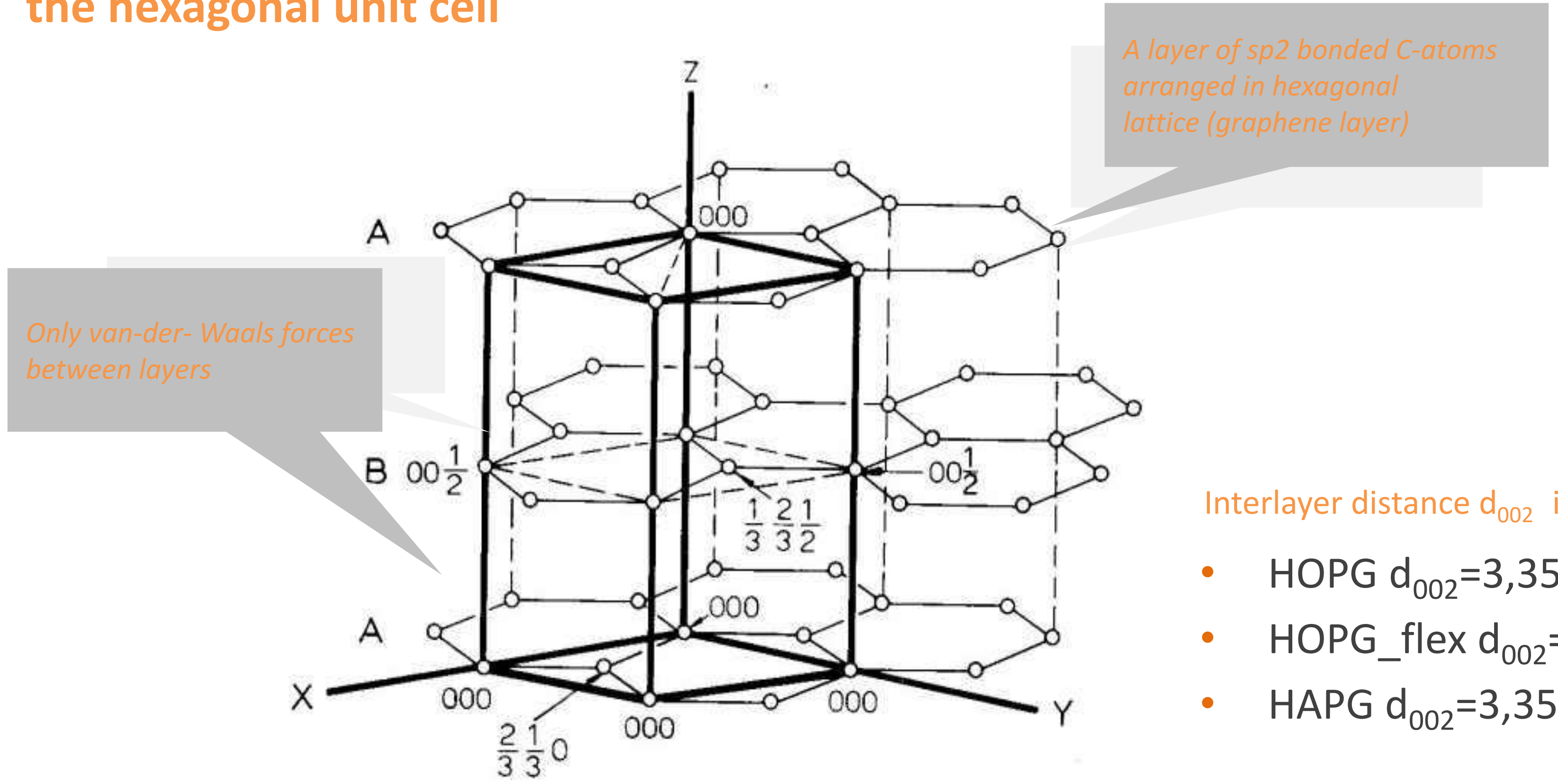
www.optigraph.eu

HPXM2021

Crystalline sell of Pyrolytic Graphite

The ideal graphite crystal structure with the hexagonal unit cell



Interlayer distance d_{002} in PG forms:

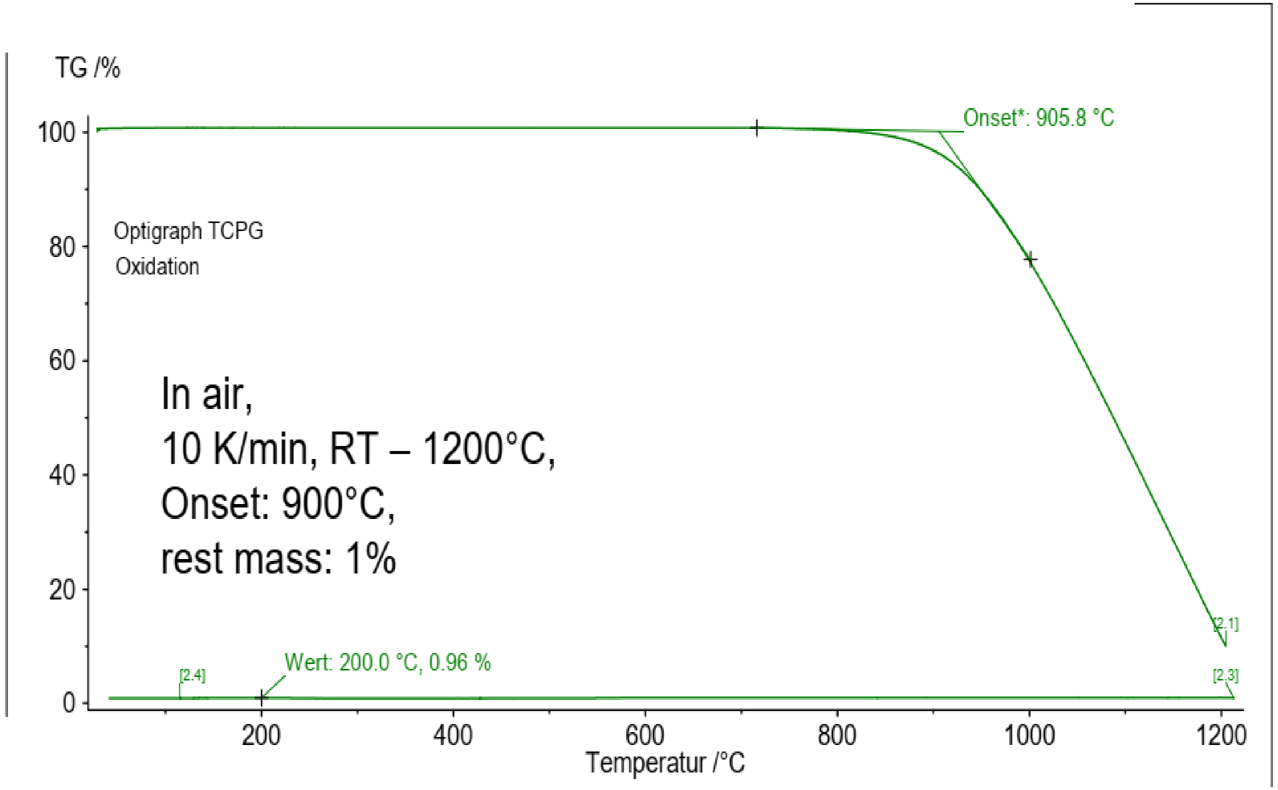
- HOPG d_{002}=3,358Å, mosaicity 0,3°-3,5°
- HOPG_flex d_{002}=3,356Å , mosaicity 0,1°-1,2°
- HAPG d_{002}=3,354Å, mosaicity 0,1°-0,2°

Unique properties of Pyrolytic Graphite

- Light material (ρ=2,26g/cm^3)
- Highest purity (99,999% carbon) predetermined by production process
- High anisotropy of structure and properties
- Thermal conductivity in plane about 2000W/mK (4 times larger than Cu)
- Electrical conductivity in plane up to $2{,}3\times10^6$ $(Om\cdot m)^{-1}$ (an order of magnitude less then for Cu and Al)
- Withstand high thermal and radiation loads : in vacuum up to 2500^{o}C , in air up to near 900^{o}C
- Chemically stable and ecologically friendly
- Unique X-rays reflectivity up to a few mrad.

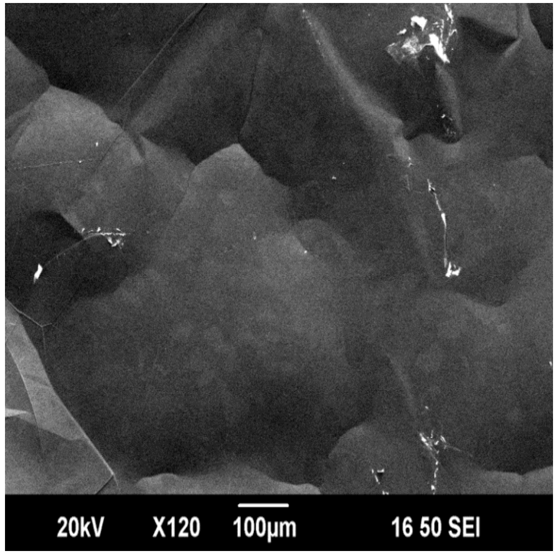
Thermal stability of PG in air

Thermal gravimetric analysis – Optigraph TCPG

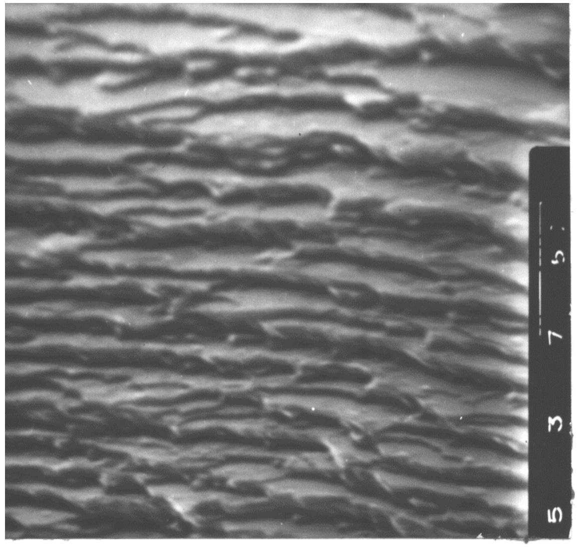


Pyrolytic Graphite starts rapidly degrade only at 900°C even in air

Grains in Highly Oriented Pyrolytic Graphite



In plane structure in SEM.
Two level structure: big blocks of a hundred µm and small crystallites of 10-30 µm



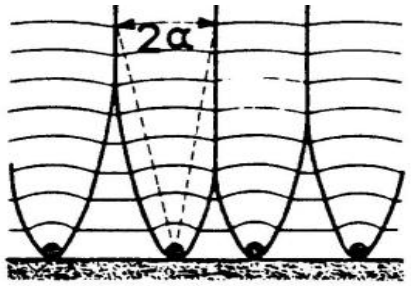
The structure of crystal edge after laser cut in SEM: the edges of the blocks of 1-3 µm thick are clearly seen

Grains boundary and interlayer defects bind the graphene layers in contrast to ideal structure

Pyrolytic Graphite: production

The first stage – production of Pyrolytic Carbon:

Thermal cracking of carbon containing gas, mainly methane and propane, on a heated substrate at T=2100°C

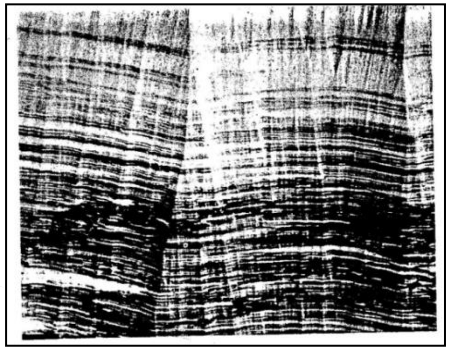


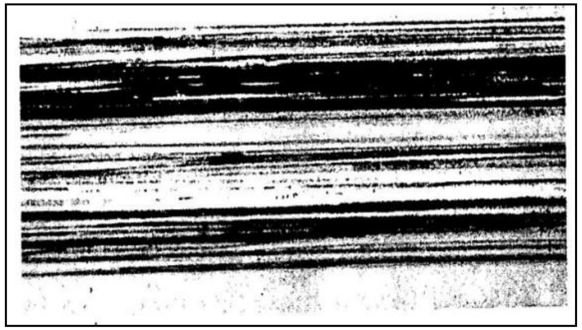
Cone structure of pyrolytic carbon

The second stage – production of Pyrolytic Graphite:

Annealing under pressure at T>2800°C

Pyrolytic Carbon only "in-plane" ordering d002 = 3,372 Å Mosaicity about 30°





Pyrolytic Graphite 3D- ordering d_{002} = 3,354-3,358 Å Mosaicity 0,4-3,5°

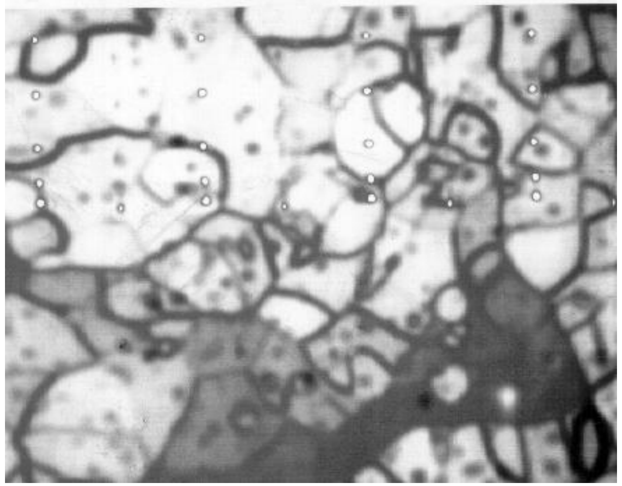
Structural changes in pyrolytic graphite during annealing under pressure.

Samples of Pyrolytic Graphite polished and etched perpendicular to the plane of deposition before and after deformation

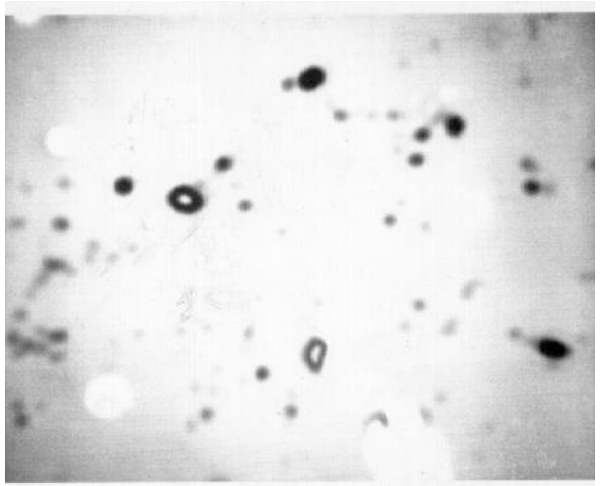
Annealing conditions determine the structure of obtained PG form

Structural difference between rigid and flexible PG forms

Special annealing procedure eliminates the vast defect regions along the grain boundary and grants flexibility to HOPG_flex and HAPG films



Commercial HOPG. Ridged material could be bent plastically at 3000˚C or elastically as a thin plate of 50-200 µm



HOPG_flex is acoustically transparent

Graphite Optics is produced by deposition of flexible films at room temperature on a polished substrate of required shape

Defects in different forms of Pyrolytic Graphite

Material	Grain boundaries	Steps	Traces of defects attributed to interlayer binding: hills, bundle, stars
HOPG standart	11	477	149
HOPG overheated (t= 3200-3300°C)	13	166	10
HOPG overheated (t=3400-3500°C)	0	181	7
HOPG flexible	3	98	17
HAPG	0	70	0

Number of defects in visual field (Averaged by 10 photos for each materials and for 30 photos for HAPG)

Measured by Olga Sinitsyna, Scanning Probe Microscopy Group of Moscow State University, Russia

PG forms commercially produced by Optigraph

Bulk (classical) HOPG

- Flat or single bent plates with a thickness up to 4mm and size app. 50mmx50mm
- Mosaic spread from 0,3 ° to 3,5 °
- Average grain size about 10 um

Used as a substrate for SPM, neutron filters, model object

HAPG

- *Flexible films* of about 10-100 µm with mosaicity of 0,1°
- Average grain size about 100 um

Used for production Graphite Optics

HOPG-flex

- *Flexible films* of about 1-10 µm with mosaicity of 0,1°
- Average grain size about 20-30 um

Used for production Graphite Optics, as stripping foils and X-ray windows

TCPG

- Flat plates with thickness up to 5mm and size up to 150x50mm
- Mosaic spread about 10 °

Used for thermal sink applications

Types of Graphite Optics

HAPG optics

Made usually from *one flexible HAPG film* up to 100 µm thick with mosaicity of 0,1 °

- Mosaic spread from 0,1 ° to 0,3 °
- High reflectivity, any custom shape , high resolution, efficient and fine focusing due to low mosaicity of 0,1 °

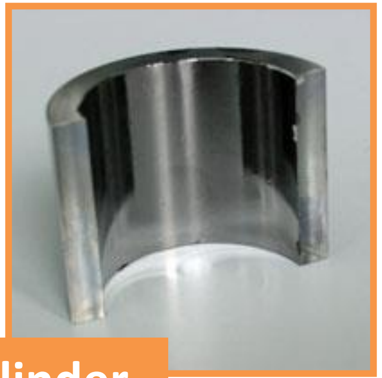
HOPG optics

- Made from *a set of flexible HOPG_flex films* of about 10 µm with mosaicity of 0,1°
- Mosaic spread from 0,4 ° to 1,2 °
- High reflectivity, moderate resolution, efficient focusing due to availability of any shape, including full figure of revolution and radii $R_{1,2}$ down to 5mm.

Optics on the base of bulk HOPG

- Made of *elastically bent* thin rigid HOPG plates 50-200 µm thick
- Mosaic spread from 0,4 ° to 3,5 °
- High reflectivity , moderate resolution
- limited shapes : only cylindrical geometry with big radius of few hundreds mm
- Problems: inner stress, shape distortion

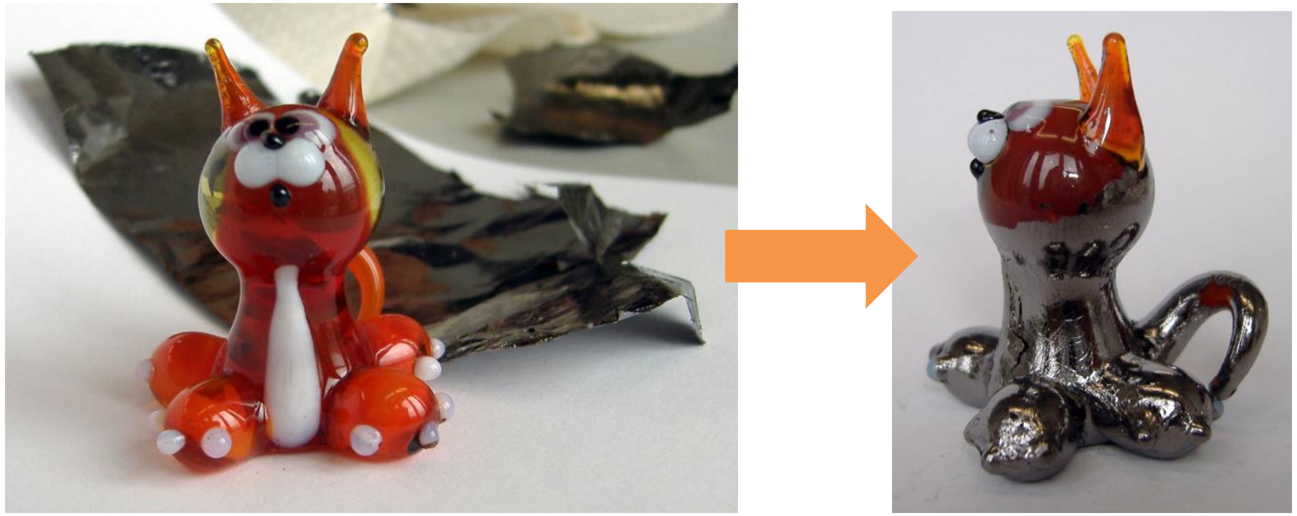
Unlimited shape possibilities of flexible graphite films



Cylinder

Ellipsoid

Log-spiral



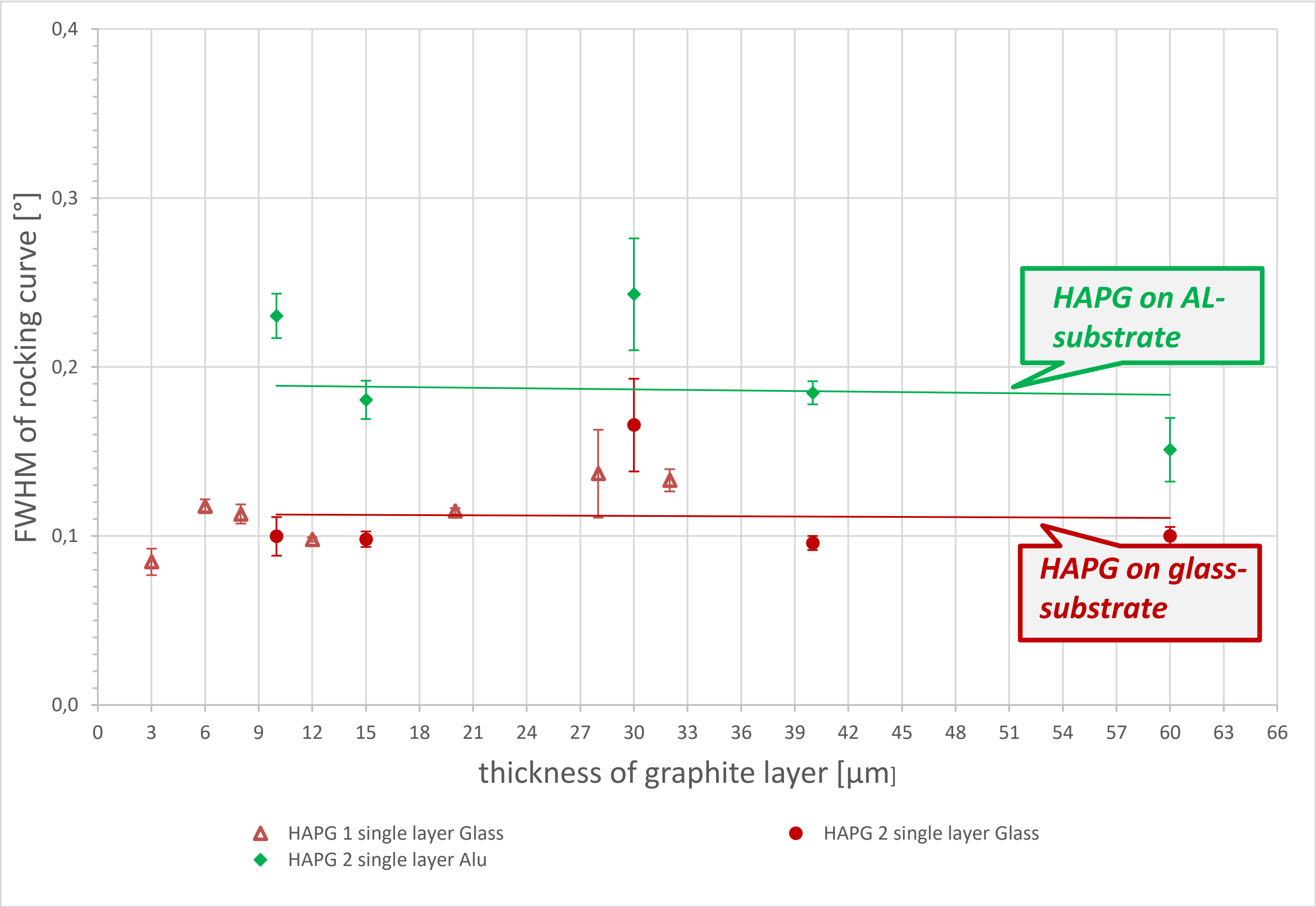
Advantages of Graphite Optics

- Outstanding stability in harsh environment. Withstand high temperature and radiation, neutron and debris frow.
- PG reflecting layer shields the substrate, spread and sink local thermal loads
- Ideal for weak signals: superior reflectivity (an order of magnitude higher than for other crystals) + efficient focusing due to possibility to make any optimal shape
- Works in hard X-rays region (2,5-60keV). The higher orders of reflection (004, 006) are bright enough for shifting the working energy toward higher energy or for increasing the crystal resolution.
- Does not loose resolution in comparison to flat crystal

In von Hamos geometry :

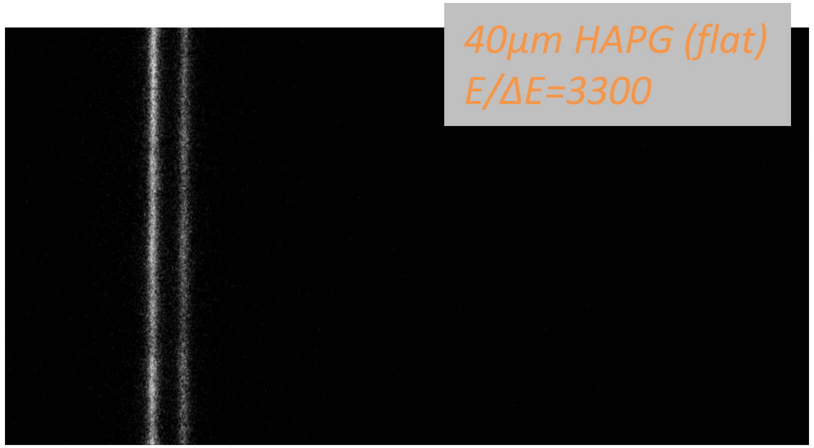
- Achieves resolution of a few eV
- Fixes spectre in one shot at energy range of 1000eV

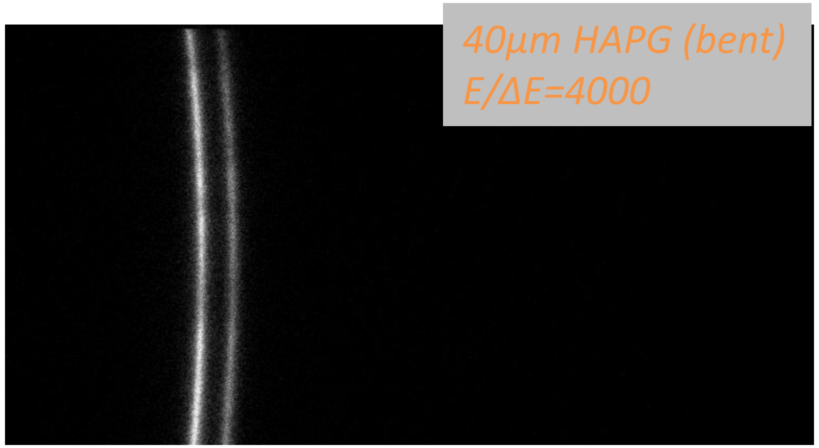
The influence of the substrate on the mosaicity (FWHM) of HAPG optics



Influence of bending on spectral resolution of Graphite Optics

distance: F = 400 mm in (004)-reflexion @ 8 keV (CuK_a)





Bending does not induce stress or distortion in the structure.
Spectral resolution of bent HAPG/HOPG crystal is similar to the flat one !

from H. Legall, H. Stiel, I. Grigorieva, A. Antonov et al., FEL Proc. 2006

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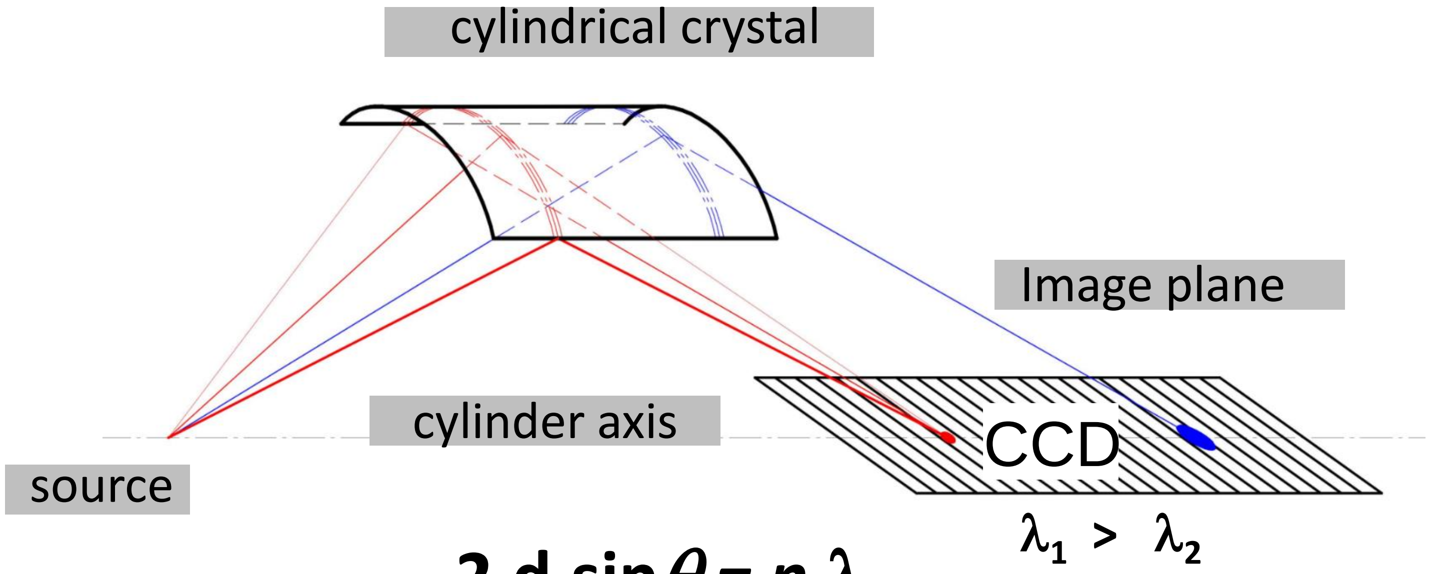
Graphite Optics in von Hamos scheme

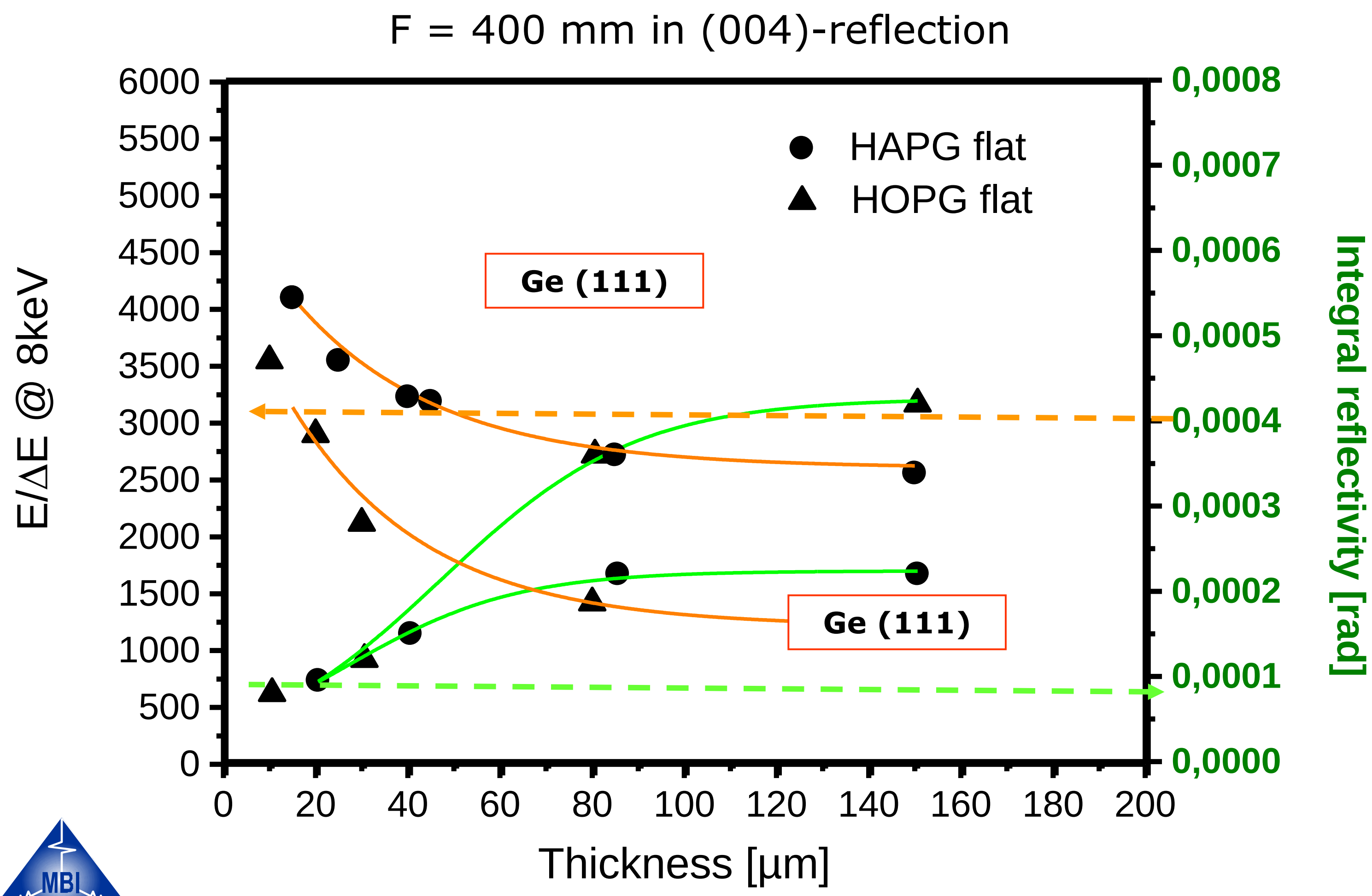


$$2 \cdot d \cdot \sin\theta = n \cdot \lambda$$

von-Hamos scheme combines mosaic focusing (parafocusing) in diffraction plane with geometrical focusing in sagittal plane

Mosaic focusing (parafocusing): when source- crystal- detector are placed equidistant, mosaic crystal provides high resolution and sensitivity simultaneously

Graphite Optics versus ideal crystal



H. Legall, H. Stiel, I. Grigorieva, A. Antonov et al. (unpublished)

Max-Born-Institut

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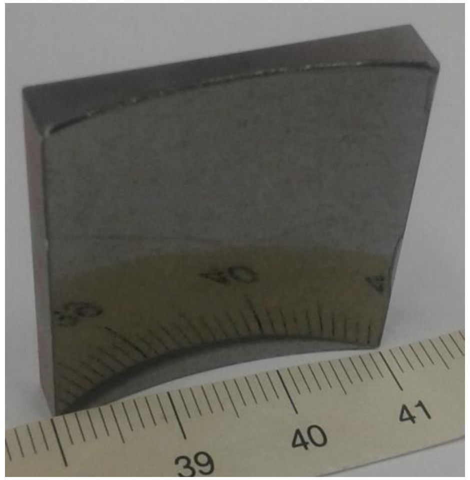
Graphite Optics for X-ray Thomson Scattering

***Conical HAPG optics for NIF, USA*.**

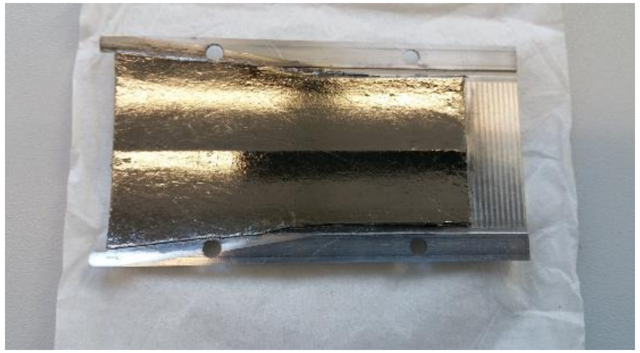
D B. Thorn et al., On the Design of NIF Continuum Spectrometer. LLNL PROC 739024 (2017)

thorn3@llnl.gov



Cylindrical HAPG optics for NTF, USA., J.Valenzuela et al., Measurement of temperature and density using non-collective X-ray Thomson scattering in pulsed power produced warm dense plasmas Nature, Sci.Reports 8, 8432 (2018)

j.valenzuela@ucsd.edu



***Dual-section cylindrically curved HOPG optics for NIF, USA*.**

Doeppner T. et al, Improving a high-efficiency, gated spectrometer for x-ray Thomson scattering experiments at the National Ignition Facility. Rev.Sci.Instr,87,11E515 (2016) **doeppner@llnl.gov**

Spectrometer with Graphite Optics becomes a routine tool for measuring temperature, density and ionization of plasma in X-rays Thomson Scattering (XRTS) experiments

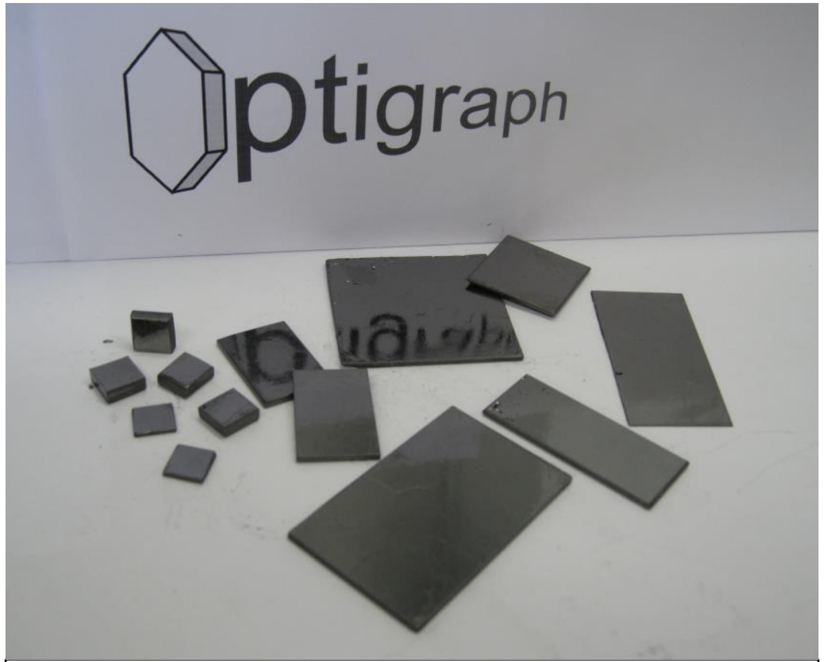
Bulk HOPG as possible pre-reflector in extreme conditions

Advantages

- Thickness up to 4 mm
- No substrate is required, a mechanical fixation is possible
- Surface can be refreshed by simple splitting of thin layers

Drawbacks

- Only flat and singly bent with big radii
- Shape distortion
- Low resolution due to mosaicity more than 0,4° and thickness aberrations

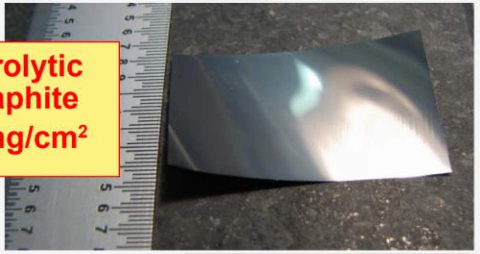


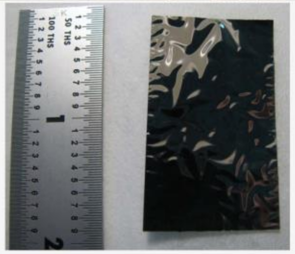
Grade	*Mosaic spread*	*Maximal size*
AgraphZ	*0,4+/-0,1degree*	*50x50x2mm*
AgraphY	*0,8+/-0,2degree*	*50x50x4mm*
AgraphX	*1,7+/-0,4 degree*	*50x50x4mm*

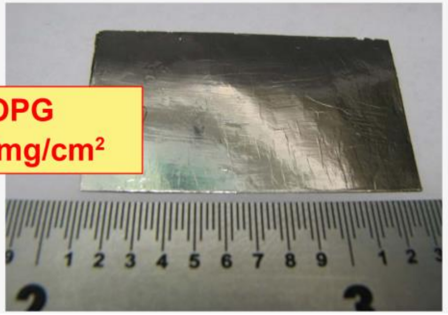
Bulk HOPG can replace Graphite Optics in the most extreme conditions, such as ITER

Stripping films for Cyclotrons

Foil and Frame Developments-cont'd







- Pyrolytic graphite of 5 mg/cm^2 was used until 2006. Thinner PG of 2.5mg/cm^2 was used in the years 2007 and 2008, and did increase the foil life but only marginally.
- Diamond foil was tried but proved to be no more reliable than the lighter PG. It was also brittle and hard to mount in the foil assembly.
- Finally from 2009 to the present, highly oriented pyrolytic graphite(HOPG) was used. This foil material has been extremely reliable, and is now used for high current extraction on all extraction probes.

FROM

TRIUMF Extraction Foil Developments and Contamination Reduction

Y.-N. Rao, R. Baartman, I. Bylinskii, V. Verzilov, TRIUMF
J.M. Schippers, PSI

CYCLOTRONS'13, Sept.16-20, 2013

X-ray transparent window for different aplications

Advantages of HOPG films:

- high purity
- their excellent thermal and radiation stability
- chemically neutral, nontoxic
- only 30% heavier than Be

❑ *X-ray transparent window of a test cell (developed PTB, Berlin) for in-situ and operando spectroscopy of energy storage materials and components*

Potential application:

❑ *Replacement of Be as a X-ray window for X-ray–tubes and detectors.*

Pyrolytic Graphite in all forms and Graphite Optics are very stable and easy to handle. Please, pay attention on this material if you need optics or thermal sink material for extreme conditions!

Thank you for attention!

Many thanks to our customers and scientific partners

for the results we partially used in this presentation for

getting you acquainted with our materials.

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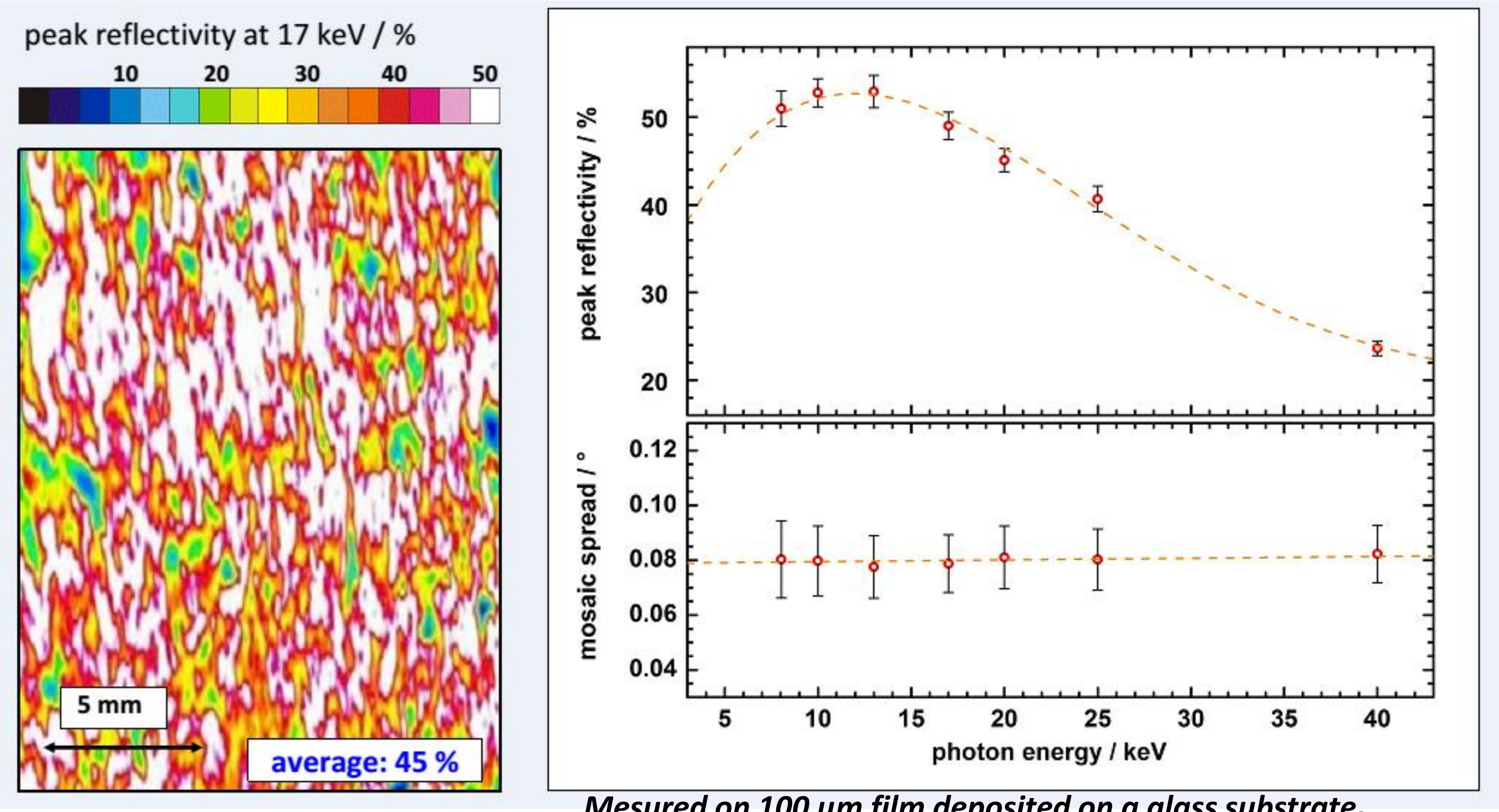
HAPG – optics for High Resolution Applications

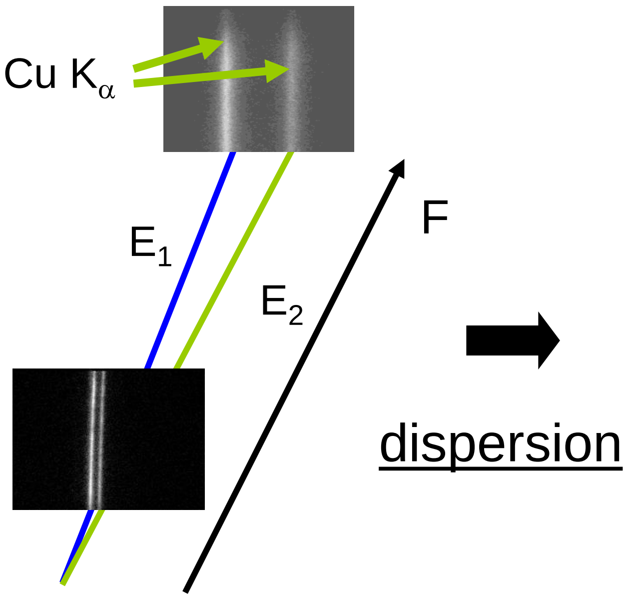


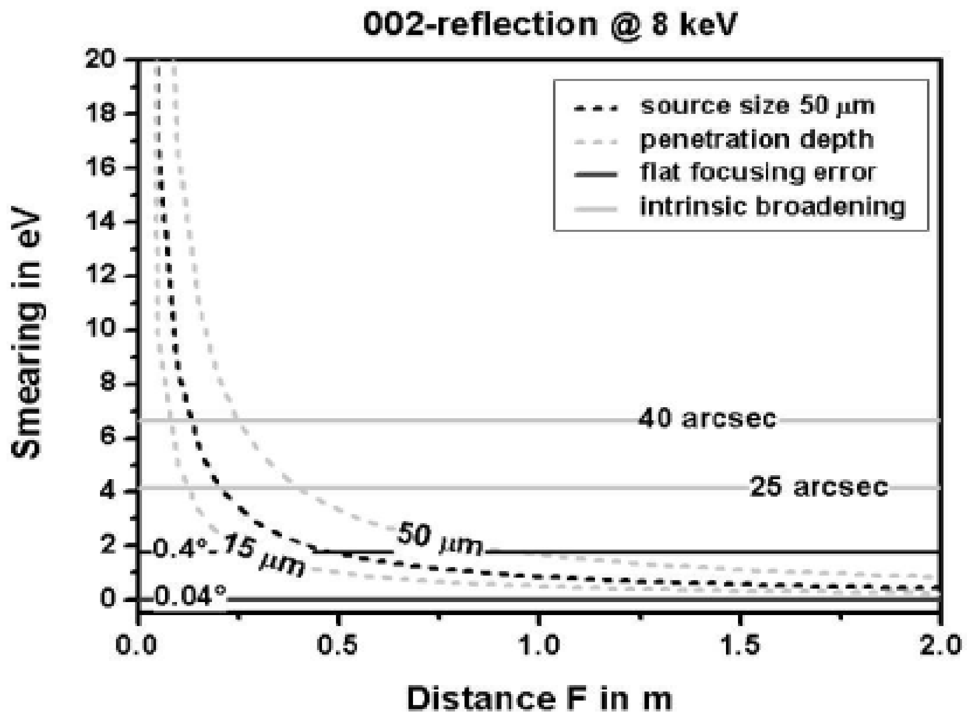
Mesured on 100 µm film deposited on a glass substrate.

A peak reflectivity higher than 45% in a wide energy range with mosaic spread of 0,08^o

M.Gerlach, B.Beckhoff (BESSY, Berlin)

Geometrical contributions to the spectral resolution decrease with distance



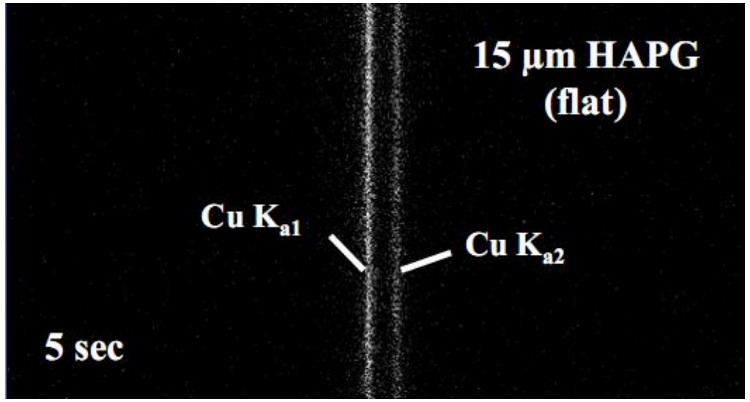


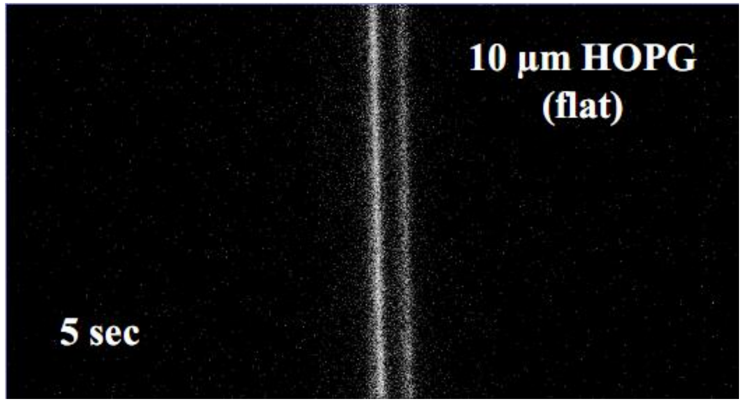
H. Legall, H. Stiel et al., J. Appl. Cryst. (2009). **42**, 572–579

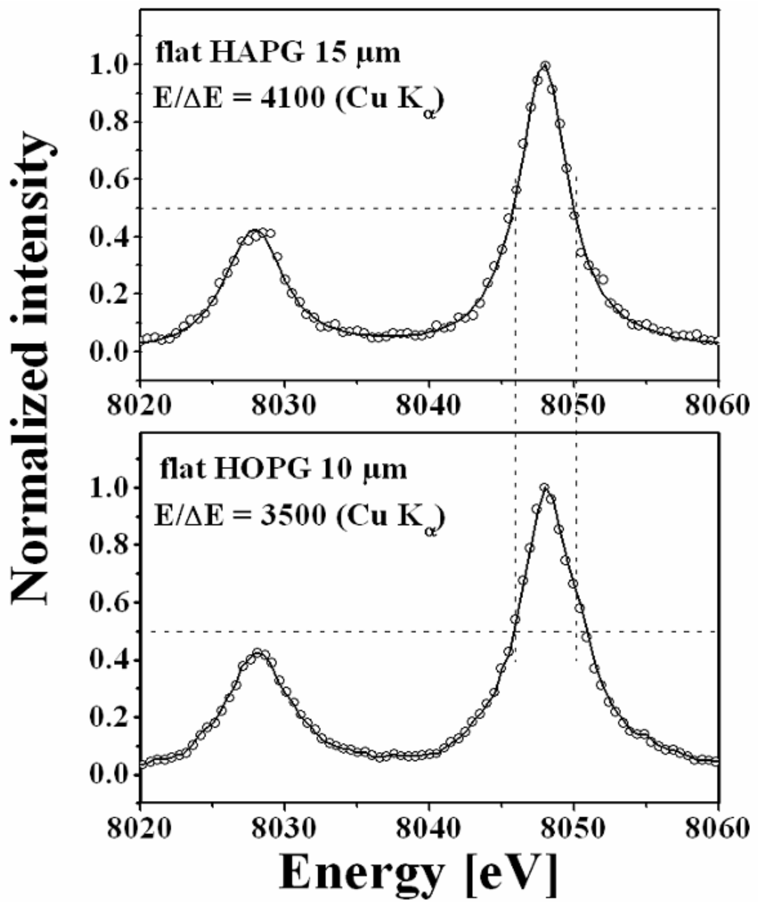
At large distances F spectral resolution is mainly limited by intrinsic broadening

Comparison of HOPG and HAPG

(004) reflection at the distance F=400mm



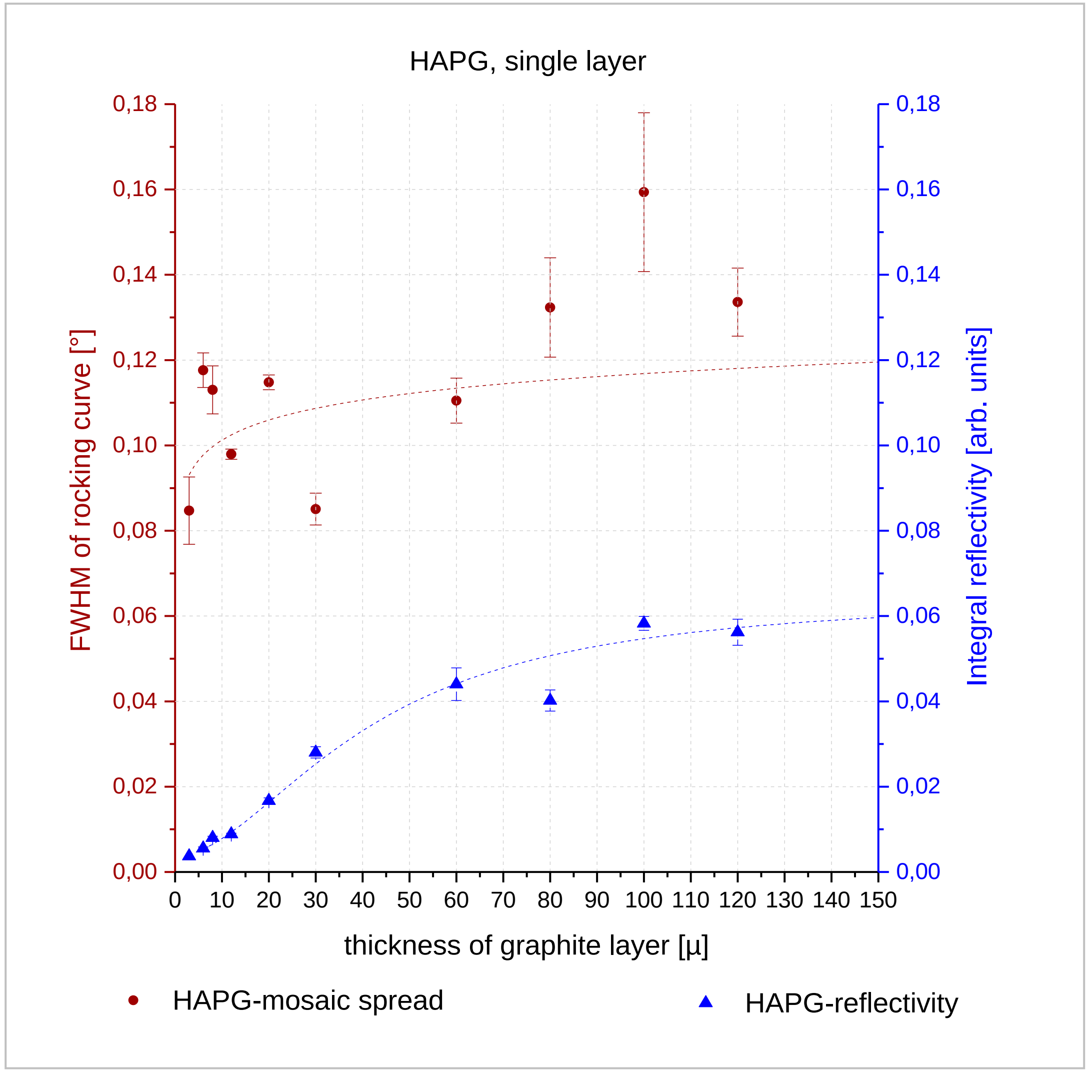




The highest resolution of E/ΔE=7000 for (004) reflection by 15µm HAPG film at the distance of 1500mm was achieved

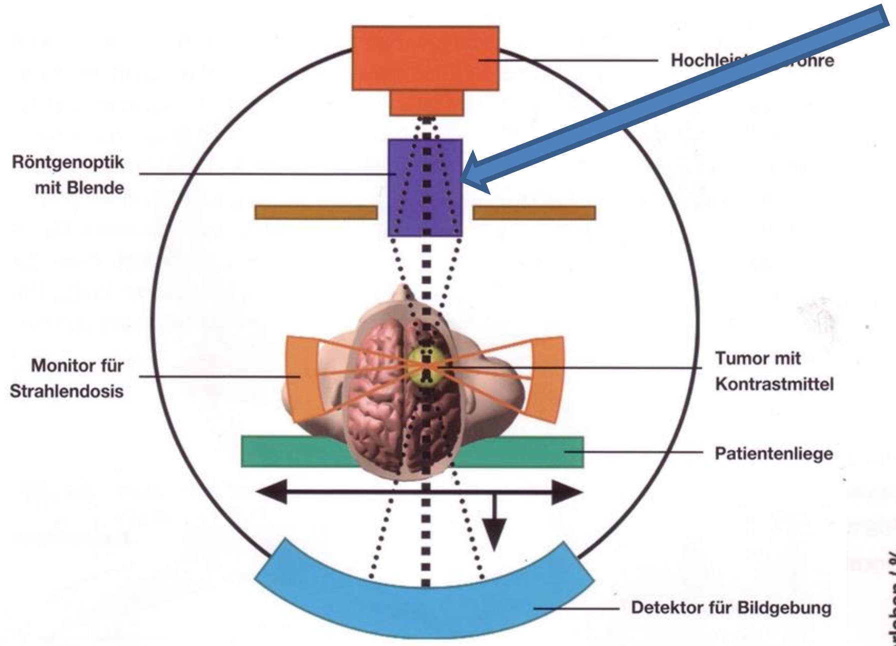
H. Legall, H. Stiel, I. Grigorieva, A. Antonov et al., FEL Proc. 2006

Mosaicity and reflectivity of Graphite Optics
HAPG optics



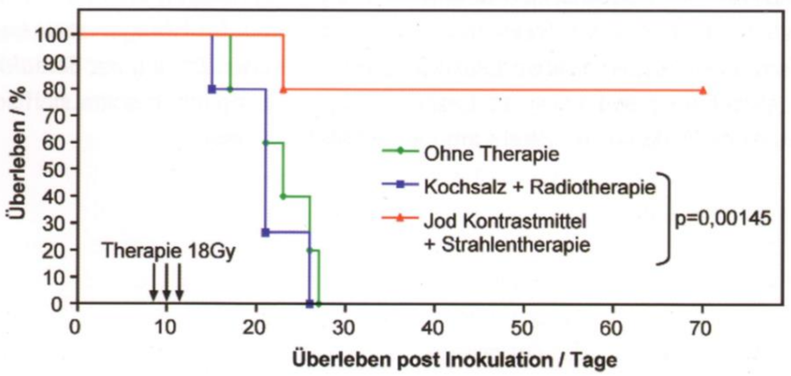
Measured on flat samples deposited on BK7 glass. Diffractometer D8 ECO ADVANCE by Bruker

Life sciences



HOPG optics of full figure of revolution collects the radiation in the vicinity of tumour and excites the low-energy fluorescence of the contrast agent. Focusing decrease the impact on the healthy tissue around.

Therapeutic effect starts after 7 min of irradiation. The longevity of patients significantly increases.



Non-invasive pharmaceutically enhanced low-energy radiosurgery

Project of Schering AG, IFG GmbH, IAP, PTB, Charite Berlin "Imaging-Therapy-Computer-Tomograph (IT-CT)", 2007