

HOPG TECHNICAL NOTE



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HOPG SPI Supplies Brand

Introduction

HOPG, is a form of high purity carbon and provides microscopists with a renewable and smooth surface. Unlike mica, HOPG is completely non-polar, and for samples where elemental analysis will also be done, it provides a background with only carbon in the elemental signature. The extreme smoothness of HOPG gives results in a featureless background, except at atomic levels of resolution. The SPI Supplies brand of HOPG should not be confused with the SPI Supplies brand of glassy carbon. HOPG is also commonly used in scanning probe microscopy as a substrate and for magnification calibration.

Lamellar structure

Graphite in general and HOPG in particular are described as consisting of a lamellar structure, like mica, molybdenum disulfide and other layered materials that are composed of stacked planes. All of these examples of lamellar structures have much stronger forces within the lateral planes than between the planes, thus explaining *the characteristic cleaving properties of all of these materials*.

Cleaving properties

HOPG because of its layered structure cleaves almost like mica. The usual approach is to take a piece of tape (e.g. 3M® "Scotch Brand" double sided tape), press it onto the flat surface, pull it off and \

the tape invariably takes with is a thin layer of HOPG. This freshly cleaved surface is what is used as sample substrate material. How many cleavings per sample? This is not easy to answer, but per a 2 mm thick block of the best grades (e.g. SPI-1 or ZYA), it is reported that one can get 20–40 cleavings. We do not guarantee a fixed number of cleavings. For the lower level grades the number of cleavings per 2 mm thickness will be less, but again just how much less we cannot predict with accuracy.

Basal plane image

In an atomic resolution scanning tunneling microscope image of the graphite structure of HOPG, there are two possible images. The image normally obtained looks like a close packed array; in this array each atom is surrounded by six nearest neighbors. The distance between any two of these atoms is 0.246 nm. Under ideal conditions, particularly if the probe tip is truly a single atom, you will see the "chicken wire" structure that shows the hexagonal rings that are the true structure of graphite; the center to center atomic distance in this image is 0.1415 nm. This distance in either case is an atomic property of carbon and it does not depend on the grade of graphite. The image shown here is the close packed array and that is the image obtained from

the basal plane of HOPG under most circumstances.

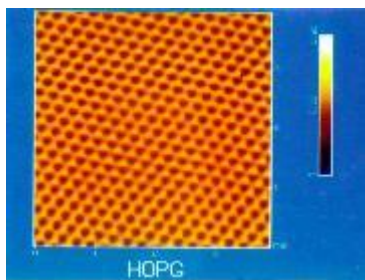


Figure 1: STM image of HOPG

Use as graphite monochromators:

The HOPG offered by SPI Supplies, especially the SPI-1 and ZYA grades, are reported to diffract x-rays and neutrons with a higher efficiency than any other material. For x-rays the intensities are increased up to five times greater than what would be possible with the lithium fluoride crystal it would replace. A singly bent focusing monochromator using these highest quality grades of HOPG, i.e. those with the smallest mosaic spread, result in intensities three times that of LiF at the same resolution.

All SPI Supplies HOPG products are suitable for monochromators except for those products that are 3mm in thickness. The uniformity of these products cannot be guaranteed through the middle of the crystal.

Flatness/Roughness

The HOPG has a structure of polycrystals, the size of which varies, the maximum being 10 mm for the highest quality. The freshly cleaved surface consists of atomic steps, 0.2–0.3 nm, and steps of several or dozens of atomic layers. The higher the quality, the less the roughness of the surface, and the smaller the number of such steps on a freshly cleaved surface.

Mosaic spread

This term is a measure of just how highly ordered is the HOPG. The lower the mosaic spread, the more highly ordered is the HOPG, resulting in a cleaved surface that exhibits virtually no steps. Lower mosaic spreads are also associated with higher

prices. However, since the lower mosaic spread material is more "cleavable", one usually realizes more "cleavings" from the more expensive material, so the increased cost is a bit less than it might first appear.

Product	Mosaic Spread	Product	Mosaic Spread
Grade SPI-1	0.45+/-0.1° degrees	ZYA	0.4+/-0.1° degrees
Grade SPI-2	1.0+/-0.4° degrees	ZYB	0.8+/-0.2° degrees
Grade SPI-3	3.0+/-1.5° degrees	ZYH	3.5+/-1.5° degrees

Table 1: Mosaic spread of two brands HOPG offered by SPI

SPI Supplies offers two different "brands" HOPG: the SPI Supplies Brand and the GE Advanced Ceramics Brand. The quality of both is excellent. Available from both brands are three grades, the top one being the "calibration" grade, the second being "research" grade which is acceptable for most experiments and a "technical" grade where less demanding material is needed, perhaps when one is mainly interested in demonstrating cleavage properties.

Use at elevated temperatures

As more and more applications are found for HOPG in research and technology, more and more applications are requiring good high temperature characteristics. We can report the following information which should be useful for those contemplating such usage:

Environment	Starts to burn Temperature
Air	500°C/932°F
Vacuum at 0.1 torr	2500°C/4532°F
Inert Atmosphere (N, Ar, He)	3500°C/6332°F

Table 2: Starts to burn temperatures of HOPG

Chemical inertness:

HOPG exhibits high chemical inertness to just about everything including osmium tetroxide. The one environment, however, where it will "disappear" quickly is in the presence of an oxygen plasma of the type generated in the SPI Supplies Plasma Prep II plasma etcher.

Columnar structure:

The structure is strictly columnar, that is, the columns run vertically within the flat slab of the material. The grain boundaries can be seen on the lateral surfaces. The mosaic spread is the angle of deviation of the grain's boundary from this perpendicular axis (of the columnar structure). Researchers in laser physics found this aspect of the information important.

Use at elevated temperatures

As more and more applications are found for HOPG in research and technology, more and more applications are requiring good high temperature characteristics. We can report the following information which should be useful for those contemplating such usage:

Air: > 500°C/932°F (Starts to burn)

Vacuum at 0.1 torr: > 2500°C/4532°F

Inert atmosphere (N, Ar, He) > 3500°C/6332°F

Calibration in z direction:

The hills and valleys on a cleaved HOPG surface are not calibrated as to their height. However, the crystallographic planes do have a definite structure and the height of a single step is 0.34 nm. Reference: L. Pauling, The Nature of the Chemical Bond, p. 235, 3rd. Edition 1960.

You may find steps randomly as a result of the cleavage process. An alternative method is to create etch pits by oxidizing the surface in an oven in air.

Ferromagnetism:

Some low levels of ferromagnetism has been observed in HOPG. This not a contamination issue but rather due to the highly ordered structure of HOPG, as compared to natural graphic which does not have such a structure.

Physical properties (at 300 K):

Density (g/cm ³)	2.27
Basal plane interlayer distance (Å)	3.354-3.358
Thermal conductivity along the basal plane (W/(m·K))	1800 ± 200
Thermal conductivity perpendicular to the basal plane (W/(m·K))	8 ± 2
electrical conductivity along the basal plane ((Ω·m) ⁻¹)	(2.1±0.1) ×10 ⁶
electrical conductivity perpendicular to the basal plane ((Ω·m) ⁻¹)	(5±0.1) ×10 ²
Purity	>99.99%

Table 3: Physical properties of HOPG