

SYNTHETIC DIAMONDS AND IDENTIFICATION

Mrs. Sharon Ferber D.G. G.C.I

INTRODUCTION

First synthetic diamonds

Diamond was discovered to be carbon in 1796, and it took more than 150 years from that time until a method of diamond synthesis was invented. The secret was pursued by many scientists but not unlocked until the 1950s, when diamond was synthesized almost simultaneously by Swedish and American researchers. Pressures of over 55,000 atmospheres and 1400C, plus molten iron to facilitate the change from graphite to diamond, were necessary.

Over the past 50 years, the uses for diamonds are multiplying and advances in synthetic production have opened the floodgates to ever more innovative applications.

The first synthetic diamonds (diamond grit) were produced in the early 1950s by researchers at the Allmanna Svenska Elektriska Aktiebolaget Laboratory in Stockholm, Sweden. The possibility of high-quality synthetic diamonds being produced for jewelry purposes, and the potential for their misidentification, have worried members of the jewelry trade since General Electric produced its first synthetic diamond in 1954. GE went on to become the largest producer of synthetic diamond; De Beers follows, with many other manufacturers also contributing to the annual output of synthesized diamonds.

The diamond industry is now facing a "new diamond age" in which synthetic diamonds have chemically, physically and scientifically become identical to a natural diamond. From what is already being man-made now, it is clear that there will be lots of uses of diamond as a material over the next 50 years. De Beers estimates the potential market for industrial diamond applications at \$50 billion, nearly as much as the \$60 billion worldwide gem diamond jewelry sales and several times the \$16.7 billion worth of diamonds in that jewelry.

Moissanite

The latest attempt to replicate the diamond is a product called moissanite. In 1893, Nobel Prize-winning French scientist Dr. Henri Moissan discovered minute quantities of a new mineral, natural silicon carbide (SiC) also known as carborundum. The mineral was located in an ancient meteorite found in the Diablo Canyon in Arizona and was later named moissanite.

It has only been recently produced synthetically, because it does not occur in sufficient quantities naturally to be commercially viable, so it was necessary to devise a way to synthesize to make it available in jewelry. Some jewelers cannot tell the difference between the colorless moissanite being sold today and a colorless diamond, so there's worry that fraudulent or inaccurate sales could take place after an initial moissanite purchase. There is a need for testing in gemological centers that have the respective lab instruments to help jewelers and others in the industry to distinguish these and other types of stones that are fraudulently represented as diamonds.

The density of synthetic moissanite is sufficiently different from diamond as to be a conclusive means of identifying it. Diamond has a density of 3.52 grams per cubic centimetre (SG = 3.52) whereas synthetic moissanite has a lower SG of 3.22. This means that by using the 'heavy liquid' called methylene iodide which has an SG of 3.33, diamonds will sink when dropped into the liquid whereas synthetic moissanite will float. This may provide a useful method of identifying a mixed parcel of diamonds and synthetic moissanites.

Another way to distinguish synthetic moissanite from diamond is to look for double refraction, or 'doubling'. Diamond is an isotropic (singly refractive) material, so it does not exhibit 'doubling.'

Commercial production of synthetic diamonds

While General Electric pioneered the diamond-creation process and has since been selling HPHT-created diamonds for industrial uses, the diamonds were not sold as gemstones until Gemesis simplified the process and was able to create much higher quality diamonds. Several companies in the US – Gemesis Corp., Chatham Created Gems and Lucent Diamond – and Sumitomo Electric, have started to produce HPHT synthetic diamonds for the jewelry market. High-quality crystals up to 3.50 ct and faceted stones up to 1.50 ct are being produced commercially. In 1990, scientists at the De Beers Diamond Research Laboratory (DRL) synthesized a 14.2 ct industrial monocrystal diamond. In 1992, De Beers's scientists grew the largest HPHT synthetic diamond of 34.80 carat for research purposes. Most HPHT synthetic diamonds are type Ib, but other types can be produced with the help of nitrogen and/or boron.

Large-scale commercial production of synthetic diamonds for jewelry has not been fully seen yet. However, the expansion of production capacity for high-quality yellow laboratory grown diamonds by the Gemesis Corp may alter the situation. Using "BARS" diamond growth equipment and expert Russian technicians, scientists and engineers from the University of Florida, the company redesigned the growth apparatus, commercialized the production and established a pilot plant in Gainesville, Florida in 2002. Over the next few years, this facility could be expanded to more than 300 "BARS" units.

According to the Diamond Trading Company (DTC), the marketing arm of diamond giant De Beers, some 200 tons of tiny synthetic diamonds, or grit, are used by the industry each year - several times total mined production. Almost all are colored crystals of up to 2ct with faceted material of up to 1ct. Synthetic diamonds are now produced with little nitrogen and as a result might not be strongly colored.

The largest crystal examined to date is a 10-carat, half-inch thick single-crystal diamond manufactured by Carnegie Institution's Geophysical Laboratory in May this year. Researchers at the Carnegie Institution's Geophysical Laboratory announced that for the first time they had succeeded to produce a 10-carat, half-inch thick single-crystal diamonds at rapid growth rates using a chemical vapor deposition (CVD) process. The Carnegie process growth rate is about 100 micrometers per hour and can reach up to 300 micrometers per hour.

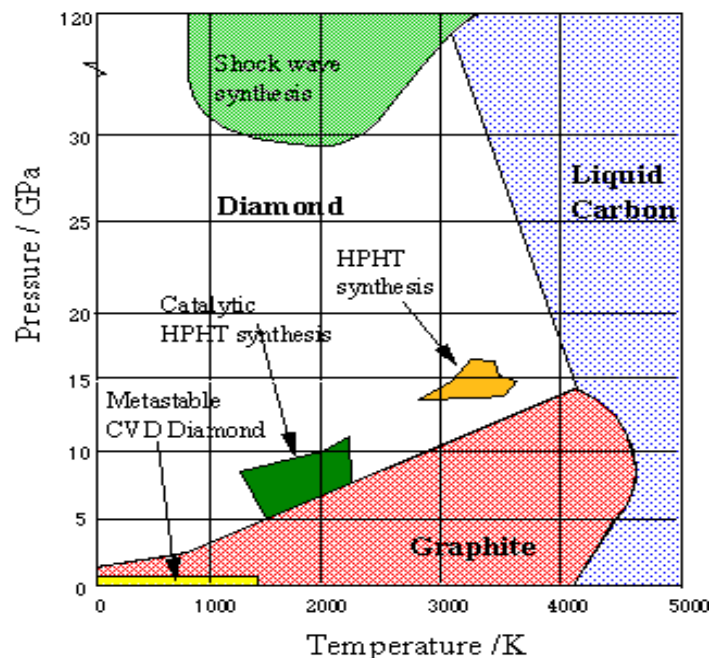
This size is approximately five times that of commercially available diamonds produced by the standard high-pressure/high-temperature (HPHT) method and other CVD techniques. In addition, the team has made colorless single-crystal diamonds, transparent from the ultraviolet to infrared wavelengths with their CVD

process.

“High-quality crystals over 3 carats are very difficult to produce using the conventional approach,” commented Dr. Russell Hemley who leads the diamond effort at Carnegie. “Several groups have begun to grow diamond single crystals by CVD, but large, colorless, and flawless ones remain a challenge. Our fabrication of 10-carat, half-inch, CVD diamonds is a major breakthrough.”

To increase the size of the crystals, the Carnegie researchers grew gem-quality diamonds sequentially on the 6 faces of a substrate diamond plate with the CVD process. By this method, three-dimensional growth of colorless single-crystal diamond in the inch-range (~300 carat) is achievable.

Synthetic diamond growth: HPHT and CVD grown diamonds



Synthetic diamonds are made of carbon atoms, organized in the same crystal lattice as their natural counterparts. As such, both have the same basic physical and chemical properties. The only way to differentiate between natural and synthetic diamonds is studying their impurities both at the microscopic and atomic level.

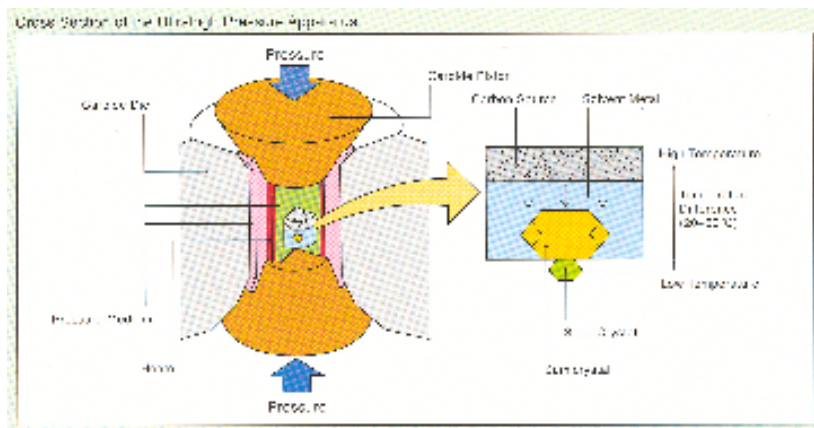
Today, high-quality synthetic and treated diamonds can be created in a laboratory using two methods. One method is growing a diamond under the High Pressure High- Temperature (HPHT) technique and the other more recent method is the Chemical Vapor Deposition (CVD). The DTC Research Centre has been at the forefront of experimental diamond treatments and the manufacture of HPHT grown and CVD synthetics to identify potential challenges for identification.

HPHT and CVD Synthesis:

HPHT grown diamonds

Although most HPHT synthetic diamonds are yellow, some have in recent years also shown large variation in color and saturation available in colorless, blue, green, orange-yellow, yellow-orange and most recently in pink. HPHT techniques can also improve the color of natural-color fancy blue and fancy pink diamonds by removing detrimental brownish undertones and thus, intensifying the color.

HPHT Process



The HPHT method uses equipment, which tries to imitate the pressure and heat-filled environment that natural diamonds are found in the depths of the earth. The HPHT method converts carbon to diamond at high temperature and pressure using a molten metal catalyst in an environment where oxygen is not allowed. The method is sometimes also used to change or enhance the colors of some rare natural diamonds, thus making them more valuable on the market.

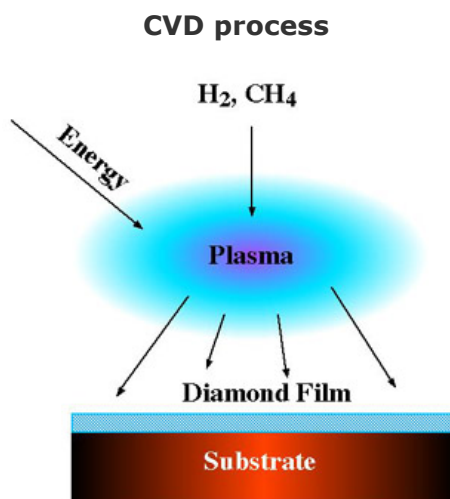
HPHT starts with a tiny diamond seed. In washing-machine-sized diamond growth chambers, each seed is bathed in a solution of graphite and a metal-based catalyst at very high temperatures and pressures. Under highly controlled conditions, the small diamond seed begins to grow, molecule by molecule, layer by layer, emulating nature's process.

CVD grown diamonds

One of the major advances in synthetic diamond technology is the CVD method, which forms diamonds through a chemical reaction between gases. In the early 1980s, a major breakthrough was made in Japan by Matsumoto, researchers at the National Institute of Research in Inorganic Materials (NIRIM) who reported CVD growth rates of over 1 $\mu\text{m}/\text{hour}$. The development led to initial interest in CVD processes and its potential industrial applications. In the late 1980s, De Beers started research into CVD diamond synthesis and fast become a leader in the field.

The CVD process involves the use of hydrocarbon and hydrogen gases and a

source of energy. The growth of synthetic diamond by CVD techniques, which do not require the extensive apparatus to generate high pressure, has been drawing increased attention worldwide. As such CVD is also a more economical method of production.



Most CVD grown diamonds are type IIa. CVD can be manipulated to make particular shapes of diamond much more effectively than the HPHT method which compresses carbon into diamond using molten metal as a catalyst. That means wafer-thin layers of diamond can be produced for use in microprocessors, or thicker diamonds for other purposes.

But the CVD process gives the producer more control over the diamond produced and, vitally, can produce colorless stones. According to Apollo Diamond, CVD will eventually produce diamonds to compete openly in the market with mined stones. Apollo started in 2004 the commercial production of CVD synthetic diamond.

The producer has reported that, initially, 5,000-10,000 carats of faceted CVD synthetic diamond will be available. Most of these goods will be quarters and thirds, but by the end of 2004, stones as large as a full carat would be on the market.

Apollo is cooperating closely with the GIA Gem Laboratory to ensure that these CVD laboratory-grown diamonds are correctly identified before being introduced into the market. The largest CVD crystal examined to date is a 10-carat, half-inch thick single-crystal diamond manufactured by Carnegie Institution's Geophysical Laboratory in May this year.

While larger sizes will be able to be identified by a selected number of professional gemological laboratories, which have the necessary testing equipment, smaller diamond sizes under a carat are often not sold with grading reports, which raises some concern. The majority of synthetic diamonds now being produced are colored stones. Most CVD diamonds are brown, limiting their optical applications. It takes longer to grow a colorless diamond than a colored diamond and as such they are less cost-effective.

Most recently, the diamond market has also seen CVD grown diamonds, which have also been subjected to HPHT color annealing for color enhancement.

Treating type IIa brownish CVD grown diamonds with HPHT can produce lighter to colorless and sometimes pinkish results.

IDENTIFICATION

HPHT grown diamonds



CVD grown diamonds



The GIA, De Beers and other laboratories have been on the frontlines doing research to develop detection techniques and products. New diamond creation and treatment technology tries to get ahead of conventional detection technology forcing gemological laboratories to use sophisticated and expensive detection methods. As a result, the ability to detect treatments and synthetics has moved from the trade to labs.

Synthetic diamonds have a number of gemological properties by which they can be identified more reliably. However, this requires from professionals in the industry and jewelers to look at diamonds more carefully than they traditionally have with the usage of standard gemological equipment. Particularly problematic for gemologists and jewelers are small stones. It is easier, faster and cheaper to grow synthetic diamonds in the form of melee. The small size though means that the visual identifying features usually are more difficult to see with the microscope.

Another concern is that the CVD technique could yield larger synthetic diamonds that might lack, for example, growth sector-related color and UV fluorescence zoning patterns. The absence of these features would make identification in most gemological laboratories more difficult.

Here are some of the most recent distinctive features to identify gem synthetic diamonds:

The morphology and growth structure of natural diamond crystals is different from HPHT laboratory- created diamond crystals. Natural diamonds have an octahedral crystal structure. HPHT grown diamonds in turn form in a cubo-octahedral structure with possible dodecahedral and trapezohedral faces depending upon the temperature and pressure used during growth.

Metallic inclusions: HPHT synthetic stones can often be picked up with a magnet because of the presence of flattened or rod-shaped black metallic inclusions. But lack of magnetic response only suggests that a diamond is natural. As CVD synthesis does not involve metal solution, metal inclusion, which is often seen in synthetic diamond produced by HPHT process, will not exist. Therefore, CVD diamond does not have magnetism, which has been announced as one of the

simple identifying features for synthetic diamonds.

Black inclusions: Graphitization of inclusions due to the high temperature employed can be indicative of synthetic origin. But one must be cautious as there are also natural black inclusions.

Color zoning: The color in the stones often grows in distinct patterns. Color zoning in synthetic diamonds is straight and angular.

Internal graining: Distinct pattern of grain lines that are seen internally and sometimes on the surface – a feature not being reported in a natural diamond. The presence of “hourglass” graining, which is usually visible through the pavilion, is proof that the diamond is synthetic. Graining is usually best viewed through the pavilion with dark field illumination.

Clouds of tiny pinpoints dispersed throughout are common in yellow to orange HPHT-grown synthetic diamonds. But clouds with a similar appearance can also occur in natural diamonds so careful examination is necessary to distinguish them.

Luminescence: Synthetic diamonds fluoresce yellow to yellowish green to both long wave and short wave UV. But short wave fluorescence stronger than long wave. This is a good indicator. In addition, when you turn the light off, sometimes a synthetic will continue to phosphoresce. The majority of De Beers synthetic diamonds exposed to long-wave UV-radiation were inert.

Electrical conductivity: The conductivity of near-colorless diamonds strongly suggests that the stone is synthetic.

Green fluorescent cross

None of these signs are definitive, but they can serve as an indication that further gemological lab testing is recommended.

An ultraviolet lamp has found to be one of the most useful pieces of equipment for identifying HPHT-grown diamonds. A microscope fixed with an UV lamp positioned overhead is necessary. When viewed under short wave UV light, yellow to orange laboratory grown diamonds usually display a yellowish green pattern with inert areas. Under long wave UV light, the intensity of the fluorescence is much weaker or inert.

CVD grown synthetic diamonds show a weak but characteristic orange with sometimes yellow-green luminescence.

The absorption and luminescence of diamonds provide key knowledge about the atomic defects present in the diamond, and is very important for detecting treated as well as synthetic diamonds.

For this purpose, a combination of spectroscopic methods - including infrared spectroscopy and photoluminescence spectroscopy – has become paramount to gemological laboratories to distinguish synthetic gems from naturally occurring ones.

Physical and optical properties in many well-grown synthetic diamonds are identical to natural diamonds. Spectroscopic properties of synthetic diamonds, however, are different from the properties a natural diamond would show. Spectrophotometers provide a way to analyze a wide range of the spectrum and objectively and quantitatively record the data by plotting a graph of results. The spectra of most natural diamonds differ from those seen in synthetic diamonds. But today, high-quality synthetic diamonds are grown, which produce graphs, which are more and more similar to the ones natural diamonds would show.

Fourier Transform Infra Red (FTIR) spectroscopy studies the absorption of infrared light. Infrared spectroscopy measures how much light a gemstone absorbs or transmits at wavelengths from 12,000 to 400 wavenumbers (1,000 to 25,000 nanometers).

In infrared spectrometry analysis, the nitrogen content and its way of existence can be detected, which is an important indication for identification for the type of a diamond (ie. Ia, IIa, etc.). The instrument is used for the determination of the colour authenticity of diamond, and proves whether it's a diamond or not.

In UV-VIS spectroscopy ultraviolet and visible light illuminates a stone and the absorption of certain colors is analyzed. In principle, the UV-VIS absorption spectrum is the scientific representation of the diamond's color. VIS spectroscopy measures how much light a gemstone absorbs or transmits at wavelengths from 190 to 1100 nm. Furthermore, the absorption graph gives indications whether a diamond has been heat treated or irradiated.

Raman spectroscopy involves illuminating a sample with a laser of a specific wavelength and a spectrophotometer is used to analyze the light scattered by the Sample. Optical centers are excited by the laser and emit a measurable amount of luminescence. The spectrophotometer shows the changes to the light as a graph. The luminescence phenomena appear as peaks in the spectrum. Photoluminescence detects certain color centers with much more sensitivity than other spectroscopic methods and is therefore especially useful for the detection of synthetic and HPHT treated diamonds.

De Beers has developed two machines, which are easy to use and can tell even colorless synthetic gem diamonds from the real thing, to prevent synthetic diamonds being passed off as mined gems.

DiamondSure is a rapid screening instrument that's been designed to pass natural diamonds, whilst at the same time referring all synthetic diamonds to further testing. Diamond Sure works by analyzing the way light is absorbed by a diamond. It's down to how nitrogen impurities form within the crystal. Nitrogen atoms occur in clumps in ninety eight percent of all natural diamonds. This causes light to be absorbed in a specific way, and provides the key to their detection. With a pass result, the user can be confident that this is a natural diamond, and requires no further testing. If the Diamond Sure machine gives indication for further testing the diamond is then referred to the DiamondView instrument.

DiamondView shines ultraviolet light on to the diamond and generates a surface fluorescence image from which synthetics may be unambiguously identified. Under ultraviolet light both natural and synthetic diamonds will glow to some degree, this is called fluorescence. But it's the patterns that are revealed by this glowing fluorescence that can tell the two apart. Strong blocky blue fluorescence patterns indicate that this is a synthetic. Such strong shapes of blue fluorescence would not be seen in a natural diamond.

Importantly, the DiamondView is also able to demonstrate to the user whether a type II stone, explicitly referred by the DiamondSure, is a potential near colorless HPHT grown synthetic. It does this by recording automatically a phosphorescence image. All near colorless HPHT synthetics show phosphorescence - an afterglow - when the ultraviolet lamps are turned off, while very few near colorless natural diamonds phosphoresce.

The new **DiamondPlus** is a compact instrument for high-sensitivity, low-

temperature photoluminescence measurements on polished stones immersed in liquid nitrogen. It consists of two solid-state lasers and two miniature spectrometers. Each measurement takes 20 seconds and results are displayed on the screen.

Conclusion

The synthetic diamond revolution could be damaging to both the consumer confidence in the integrity of the natural diamond and the diamond industry as a whole. As the technologies for the manufacture of synthetics and the treatment of diamonds becomes more sophisticated and widespread the diamond industry requires multiple solutions for the development of easy-to-use instruments, mainly for use at gemological laboratories designed for the disclosure of synthetics, treated diamonds and diamonds simulates. The challenge to the industry itself remains the awareness of gemologists and laboratories to keep up with the latest machines and instruments and for individual players to be aware of the need for gemological testing.