

# Invisible diamonds: diamond at the nanoscale

Since the early 1900's chemists, physicists and industrialists have had a need for a material that was multifaceted. Diamond is one of those materials that can be beneficial in a wide range of applications such as jewellery, machinery and medicine. In the last five to seven years diamond has taken a new form. Its size has decreased from centimetres to millimetres to microns and now to nanometres. Nanometre sized diamond in low concentrations is invisible to the naked eye. In general, diamond can be found in two basic forms – monocrystalline and polycrystalline. This article by R. Abramshe, will focus on the polycrystalline form of nanoscale diamonds.

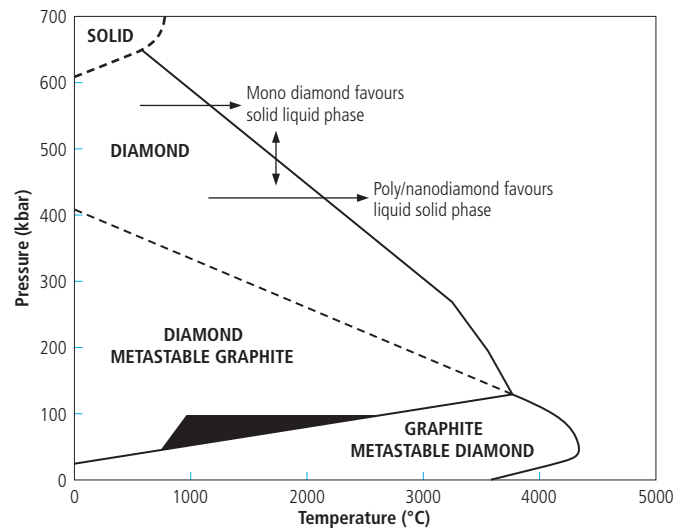


Fig 1 Berman-Simon phase diagram for diamond/graphite

Diamond and graphite are different forms of crystalline graphite. It was widely believed at the beginning of the twentieth century from geological studies that diamonds were formed very deep in the earth where both temperature and pressures were very high.

From the third law of thermodynamics as proposed by Nernst in 1906 it was possible to make the necessary calculations to reach proper equilibrium for crystalline graphite to convert to diamond. From that point there was a slow but steady progression of individuals who theorized the estimates of the temperature, pressure curve for conversion.

Berman and Simon calculated a full conversion line of graphite to diamond in 1955 using reliable data for the lower limits of conversion and subsequently the higher regions of conversion (Fig 1). This is deemed important because the curve suggests that synthetic diamond could be converted at room temperature with high pressures. However synthetic diamond is not thermodynamically stable at room temperature even though it does not convert back to graphite at room temperature.

This is because carbon-to-carbon bonds, which require a great deal of energy to break apart, hold the atoms of both forms of carbon together. The required energy on the average is  $10^{10}$  Newton metres<sup>-2</sup> for sized diamond at 35/40 US mesh. The stability region of diamond synthesis is above 1,800 Kelvin at pressures exceeding 60 kbar.

## Early synthesis

The pressures and temperatures were initially obtained by a type of press developed by Bridgeman who made a series of presses and experiments in several failed attempts to synthesize diamond.

A later press, designed by H. Tracey Hall, is one where a reaction chamber is surrounded by cylindrical electrical heaters, which in turn are surrounded by a ceramic cylinder which acts as an insulation barrier. This cylinder is then compressed between tungsten carbide anvils. The cylinder is then encapsulated in an annulus of tungsten carbide, which is further constrained by steel "belts".

One of the most critical features of this type of press is the gasket at the top of the cylinders. This criticality stems from the fact that the gasket materials must withstand the pressure and heat generated by the anvils and must be able to transmit electric current though the internal capsule containing graphite and catalyst.

From the 1950s onward, this type of high pressure/high temperature system was used to produce the majority of monocrystalline synthetic diamond that is used for industrial purposes.

## Polycrystalline diamond

The Du Pont Company in the 1960s was looking for new ways to use their explosive products. They calculated that one could decrease the process time of making diamond with an explosive shock wave. The pressure and temperatures could be achieved and exceeded. A problem with this method was how to control the reversible reaction due to the high energy required by the explosive mixture. They uniquely used a copper core within their explosive device to cool the reaction after the synthesis of diamond.

The process methodology to synthesise poly diamond is to use crystalline graphite and a catalyst. This mixture is packed around a copper tube. This is encased in a stainless steel tube which itself is encased in a hardened steel tube packed with explosives. The tubes are then projected at a target. Upon striking the target

the resultant explosion rapidly converts the graphitic carbon to diamond. Because of the rapid cooling due to the copper core, conversion to monocrystalline diamond is stunted and a resultant polycrystalline crystal substructure is formed. The crystallite sizes of the poly crystallites are between 22 and 66 angstroms. Above 66 angstroms the poly diamond begins to lose its identity as a polycrystalline diamond. Above 108 angstroms it acts much like monocrystalline diamond.

A base definition of a nanoparticle is, any material consisting of grains of particle sizes that are 1 to 100 nanometres in size. These materials would belong to the nanostructure family.

### UDD species of diamond

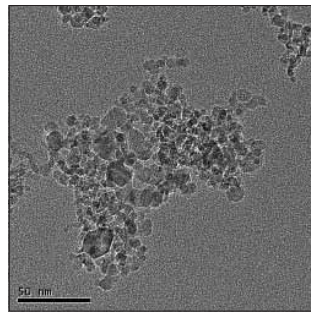
Ultra dispersed (or ultra detonated) diamond (UDD) is produced by the detonation of an explosive mixture in an oxygen deficient atmosphere. UDD has undergone a general shock loading, meaning rapid rise in pressure and temperature from the explosive process. A condition of 30 GPa at 1,000 to 2,300 °C is the general form of production. The result produces thermodynamically stable diamond powder which contains agglomerates of 50 nm to 5 µm. These agglomerates contain individual crystallites of 2 - 7 nm. A small fraction of these crystallites can be up to 10 to 50 nm crystals.

### Production

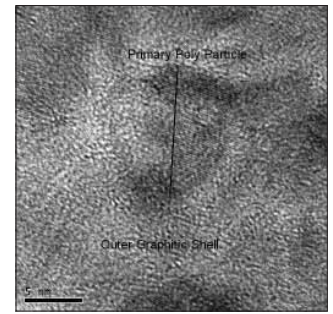
Three methods, all involving an oxygen-deficient process, can be used to produce UDD particles. The first process involves an explosive mixture (small charges) that is detonated in a reaction chamber in the presence of a blend of inert gases (the chamber design and gas loading is a propriety mix.) The result is UDD diamond with a percentage of primary particle and secondary particles. The surface composition is affected by the gas composition and chamber design. In general, this process produces the highest concentration of complex surface carbons of different species. The second process uses a modification of the inert gas process, where an explosive mixture of TNT and hexogen is detonated in a reactor chamber filled with inert gases and water. The main difference involves the secondary particle size and its surface composition. Water cools the explosive gases more rapidly, producing a more-ordered carbon surface structure that makes it possible to predict results in some applications. A modification of the first two processes, the third method uses a different blend of explosives, a large reactor chamber and ice. The explosive charge is encapsulated in a solid block of ice and is detonated under water with an active water spray. The resultant product provides for a different surface group on the secondary particle. In terms of creating a more ordered structure, this particular method provides a higher degree of ordered surface carbons and chemistry. Predictability is a key to reliability. For some processes that utilize nanodiamond, this predictability is essential to the desired outcome.

### Processing

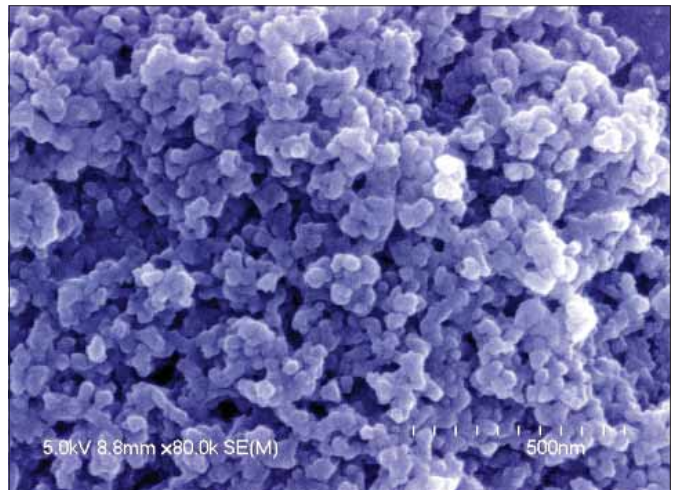
The recovery of the nanodiamond particles from the explosive detonation material requires treatment with reducing and oxidizing chemicals. Combinations of alkalis and mineral acids are used separately in conjunction with heat. This process is necessary to remove metallic, physically adsorbed and chemically absorbed explosive residue. The approximate yield of usable nanodiamond is roughly 90 - 97%. The 3 - 10% of removed undesirable material consists of 80 - 89% total carbon and 2 - 8% C-O, C = O.



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*Fig 2a Primary particles forming UDD clusters*



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*Fig 2b UDD particle surrounded by graphite outer core*



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*Fig 2c Example of nanodiamond clusters in a dried powder*

### Final product

Fully recovered and processed UDD powders contain both primary particles and secondary particles (Fig 2). A primary particle is defined as the base particle that comprises the larger particle in the aggregate. Much like atoms forming molecules, molecules forming substances, substances forming things, e.g. carbon and hydrogen atoms (primary particles) forming long chained hydrocarbons linked together to form crude oil. Primary particles have crystallite sizes on the average of 4 nm and range from 2 - 7 nm.

Secondary particles are defined as the aggregate of the primary particles that are put together in an ordered fashion to form a cohesive part. They can be considered as clusters of the primary particles with an outer coating of graphite, graphene and other forms of carbons as carbon onions and tubes as well as some quasi-amorphous carbon.

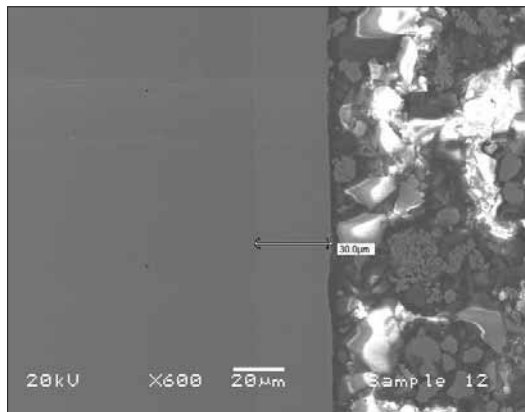
### Applications for UDD

Nanodiamond (ND) particles synthesised by explosive detonation, each the size of a small virus and less than 1,000 times the thickness of a human hair, have drawn considerable attention in the past few years. In addition, the recent development of UDD nanodiamond production at a commercial level makes it possible to utilise ND's physicochemical properties in the field of nanotechnologies. Nanodiamonds (unlike monocrystalline diamond) are hydrophilic (will hydrate with fluids including water), owing to their high surface-to-volume ratio. The ND core consists of the  $sp^3$  orbital crystal structure, and the surface has the  $sp^2$  orbital structure along with hybrids of  $sp^2/sp^3$ . Therefore, the surface contains a complex arrangement of carbons throughout the cluster.

## Polishing

From an intellectual perspective, nano-particles open new vistas in micro machines, medical applications and in new frontiers of industries such as electronics, coatings and optics. Some examples are given below:

- ◆ Any application where super finishes are required, such as the polishing of optical devices used in telescopes, laser windows and extraterrestrial vehicles for space exploration.
- ◆ Next generation of diamond cutting tools (Fig 3). With its more uniform and ordered microstructure, nanodiamond can be used to increase the wear resistance of drills. Cutting tools can be made sharper and produce better finishes while lasting longer when machining tough metallic objects like titanium or when used in deep oil and gas exploration.



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*Fig 3 Example of nanodiamond deposition on tool steel – 30  $\mu\text{m}$  diamond coating gives a threefold increase in hardness (Vickers)*



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*Fig 4 A selection of parts that have been plated with nanodiamond for practical applications*



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*Fig 5 Sapphire components finished using nanodiamond in CMP polishing operations*

- ◆ Densification of other materials made from aluminium, boron nitride, boron carbide and magnesium oxide/niobium oxide combinations. Here the applications become almost unlimited. Some examples would be a fully dense but lightweight armour or as filler for cermets in the structural ceramics industry.
- ◆ Fixed polishing applications, such as polishing films and polishing pads for fibre optics applications. Nanodiamond can increase the usable area of silicon carbide wafers by removing defects.
- ◆ Nanodiamond is a biocompatible material and, because of its small size and ability to “carry” medications into human cells without inflammation, it is becoming a promising new material in medicine. Already, it has been used as a carrier (delivery system) of medications for treating tumours.
- ◆ Nanodiamond can be used in electrolytic and electroless plating applications with very little modification to the process (Fig 4). It has been suggested that the effect of ultra dispersed diamonds results in hardness, strength and fine structure with respect to current density and diamond concentration in the electrolyte. Potential application of the coating is sliding bearings, insulators, medical appliances and aerospace parts.
- ◆ Advanced Chemical Mechanical Planarisation applications to polish sapphire, SiC, GaAs, GaN and other compound semiconductors to unprecedented levels of precision (Fig 5), while improving surface integrity (i.e. removing sub-surface damage, cracks or micro-cracks) obtaining surface finishes of less than 2 nm on various A, C, M and R plane sapphire for optical or electronic applications. The same finishes can be obtained on silicon carbide wafers for IC memory devices.
- ◆ It has been shown that small additions of functionalised nanodiamond to a polymer matrix can lead to positive modifications leading to essential improvements in rheological, mechanical and tribological characteristics.

### Examples of UDD in industry

It is worth looking into a few application examples in more detail to give an indication of the possibilities for nanodiamond across a broad range of industries:

#### LED polishing

A light-emitting diode (LED) is a semiconductor light source. LEDs are used as indicator lamps in many devices, and are increasingly used in applications as diverse as replacements for traditional light sources in aviation lighting, automotive lighting (particularly indicators) and in traffic signals. The compact size of LEDs has allowed new text and video displays and sensors to be developed, while their high switching rates are useful in advanced communications technology. Infrared LEDs are also used in many commercial products such as a TV remote.

The LED is based on the semiconductor diode. When a diode is switched on, electrons are able to recombine with holes within the device, releasing energy in the form of photons or light as we more commonly call it. They are becoming increasingly popular because of their versatility and low energy consumption compared to standard lighting devices.

## Polishing

A new type is the organic LED or OLED. The organic material within them is usually a polymer, which makes them very thin and flexible. Already, OLEDs have been used to produce visual displays for portable electronic devices such as mobile phones, digital cameras, and MP3 players and there is great potential for their future use in large format HD TV flatscreens, wall displays or even as luminous cloth.

No matter which type of LED (Figs 6, 7 and 8), the quality of light emitted depends very much on the quality of the final polished surface of the glass or ceramic substrate. This is an area that has great potential for producers of UDD.

### Sapphire polishing

#### General principles

An application where ND can have an immediate impact is in the final stage of sapphire polishing. It is important to note that the economic value of polishing is dependant not only on removal rate, but on a host of other process outputs such as finish, reject rate, production time required, and sub-surface damage. Variables in the sapphire polishing process include the speed of the machine (rotational) in rpm, the type of pad used on the platen (soft to hard), pressure (low to high), rotation (clockwise or counter-clockwise), back pressure on the workpiece, slurry composition, and drip rate. While some of these variables can be defined, the actual dynamic is in the interaction of the workpiece (in this case, sapphire), the ND-containing slurry, and the pad. Physical properties of the fluids are important as they affect both fluid dynamics and material transport in polishing. These properties, including viscosity, density, pH, solids concentration and thermal stability, can also be varied by changes in the chemical composition of the slurry. Particle size affects the number of particles in the slurry if weight percent concentrations are used. For small-diameter particles, a given slurry weight percent contains more particles than for large-diameter particles. The agglomeration of smaller particles can occur under certain conditions. If these agglomerations are due to van der Waals forces, they are considered "soft" agglomerates and may not be important.

If the agglomerations are a result of a chemical interaction of the particles in the makeup of the slurry, however, they become more important because this phenomenon affects average particle size and size distribution. In some cases, the agglomerates become hard and then fracture, thereby changing the average particle size and shape during the polishing process. This usually leads to defects and rejects. The shapes of different particles may be significant. Some particles are characteristically spherical, but elliptical, blocky and sharp/fractured shapes are also used. Concentration effects may be negligible in some polishing operations or significant, as in CMP. Concentrations of solids may be given as weight percent or particles per volume. As previously mentioned, in sapphire CMP, the type of slurry, particle and pad become the dominant variables. Many volumes of work have reported on the mechanisms of removal when the particles are harder than the workpiece. With a nanodiamond addition to colloidal silica in sapphire CMP, the mechanism is somewhat similar. The applied load is born by particles embedded in the lap system in conventional polishing, while, in CMP, the applied load is born by the pad. Each abrasive particle removes material independently. At high concentrations, the removal rate tends to reach a peak limit as the pad becomes saturated. At low concentrations, each particle has an equal chance of embedding into the lap and the polishing rate increases with concentration. As the particle embeds into the lap, material

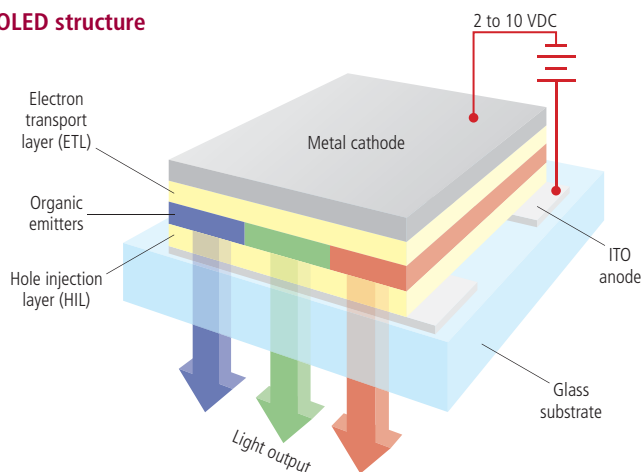


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Fig 6 Super polishing of silicon on sapphire for LED applications



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Fig 7 An ultraviolet LED – a more highly polished ceramic substrate surface will emit more light for the same energy input

### OLED structure



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Fig 8 Super polishing of the glass substrate in an OLED will increase the light output at the same power level

removal can be considered from the perspective of classical cutting mechanics. If the spacing of granules is sufficient, removal rates are controlled by the cross-sectional area of the material removed. For soft laps (or for the soft polyurethane foam pads used on laps in CMP), sub-micron diameter abrasives can be pushed deep into the lap, flexing and rebounding of the lap surface to make direct contact with the workpiece and carry most of the applied load.

The number of active particles is the product of the contact area and the number of particles per area of lap surface. In addition to the variables discussed above, pad roughness and abrasive size distribution also have an effect. Increasing the width of the particle distribution brings two countervailing effects. A reduction in the number of particles in the mean of the distribution where a considerable amount of work is done can either reduce material removal rate for small mean particle sizes or increase the removal rate with a potential loss of surface quality with a larger proportion of large particles. ND is in the same size regime as colloidal silica and ceria slurries, with sizes ranging from 20 to 100 nanometres. Any potential surface damage is mitigated by ND's unique clustering. The use of ND in CMP or fine polishing to the angstrom level eliminates many of the associated problems of sub-surface damage and heat buildup that can be encountered when using conventional single-crystal poly-particles processed to nanometre size ranges

## Case Study

A trial was conducted at a watch glass manufacturer in Switzerland using 100 nm ND particles in colloidal silica for the final CMP of R-plane sapphire watch glass. The purpose of the study was to identify either increased production rates or quality improvements using ND in a percent replacement for colloidal ceria or silica. Kostosol 3550 silica was used, along with a 5% by weight blend of nanodiamond in a chemically compatible fluid. The polishing pad was manufactured by Rodel and had a Shore A rating of 90, and the machine manufacturer was COMES.

For the initial test, the cycle time was 4.5 minutes at 3.5 bar. The R-plane sapphire pieces were 35 mm in diameter, and four pieces were used per run. (Results are shown in Table 1.) The test was then duplicated on 42 mm diameter wafers with two pieces per run (see Table 2), and again using the same size of sapphire wafers with four pieces per run (see Table 3). The next test was a re-polishing to remove scratches (rejects) from pre-CMP polish defects. For this test, the sapphire pieces were 36 mm diameter with four pieces per polish (see Table 4).

In all cases, the use of ND showed a beneficial effect on both quality and the potential to reduce manufacturing time. In addition, the ND suspension was stable for one month. These results have been duplicated at another sapphire watch maker as well. Colloidal silica and ceria are soft materials, and part of the polishing action using these agents occurs through a surface chemical process. The tribo-chemical wear process in CMP and CMP-like operations, which is difficult to control, takes place in the action interstice between the pad and workpiece. When polishing operations are conducted on the functional surfaces of brittle media, the surface of the medium to be polished, the polishing agent and the carrier of the polishing agent are all factors.

The suspending fluid also exerts considerable influence on the level of wear sustained by the pad/piece. To date, it has not been possible to develop a hypothesis that combines all of these aspects, though it is known that the polishing process is determined by the reactions that take place at the contact surface between the workpiece and the polishing medium in aqueous solutions. The addition of ND, even in small quantities, provides particles with a hard core surrounded by a functionalised cluster that, in effect, provides a "burnishing" to the workpiece. The end result is that sapphire or other substrates are pseudo-mechanically polished to a high degree. In addition, the chemical process is muted and time reductions are possible using a tailored ND.

## Summary

This article has shown that nanodiamond should be considered for the final polishing of any substrate where the tribology of the substrate is critical. In addition to the reduction of subsurface damage and increased surface finish, it is also possible to increase productivity and reduce costs through the introduction of nanodiamond.

In addition to polishing, nanodiamond also has potential for use in many other areas such as medical, wear parts and cutting tools. ♦

### ♦ Author

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Trial	Time	Pressure	Quality	Conditions
1	4.5 min	3.5 bar	OK	standard
2	3.8 min	3.5 bar	OK	10% time improvement
3	3.2 min	3.5 bar	OK	30% time improvement
4	2.7 min	3.5 bar	OK	40% time improvement
5	2.0 min	3.5 bar	OK	50% time improvement

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*Table 1 Results of the initial test of 35 mm diameter sapphire wafers with four pieces per run*

Trial	Time	Pressure	Quality	Conditions
1	5.0 min	3.5 bar	OK	standard
2	2.0 min	3.5 bar	OK	60% time improvement
3	1.5 min	3.5 bar	OK	70% time improvement
4	1.0 min	3.5 bar	OK	two small circular scratches noted

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*Table 2 Results of second test, which used 42 mm diameter wafers and two pieces per run*

Trial	Time	Pressure	Quality	Conditions
1	5.0 min	4.0 bar	OK	standard
2	1.5 min	4.0 bar	OK	70% time improvement
3	1.0 min	4.0 bar	OK	80% time improvement
4	0.5 min	4.0 bar	OK	two pieces had orange skin

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*Table 3 Results of third test, which used 42 mm diameter wafers and four pieces per run*

Trial	Time	Pressure	Quality	Conditions
1	2.0 min	4.0 bar	OK	Could not do with colloidal silica alone
2	1.5 min	4.0 bar	OK	Could not do with colloidal silica alone
3	1.5 min	4.0 bar	OK	Removed all scratches

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*Table 4 Results of re-polishing test, using 36 mm diameter wafers and four pieces per polish*