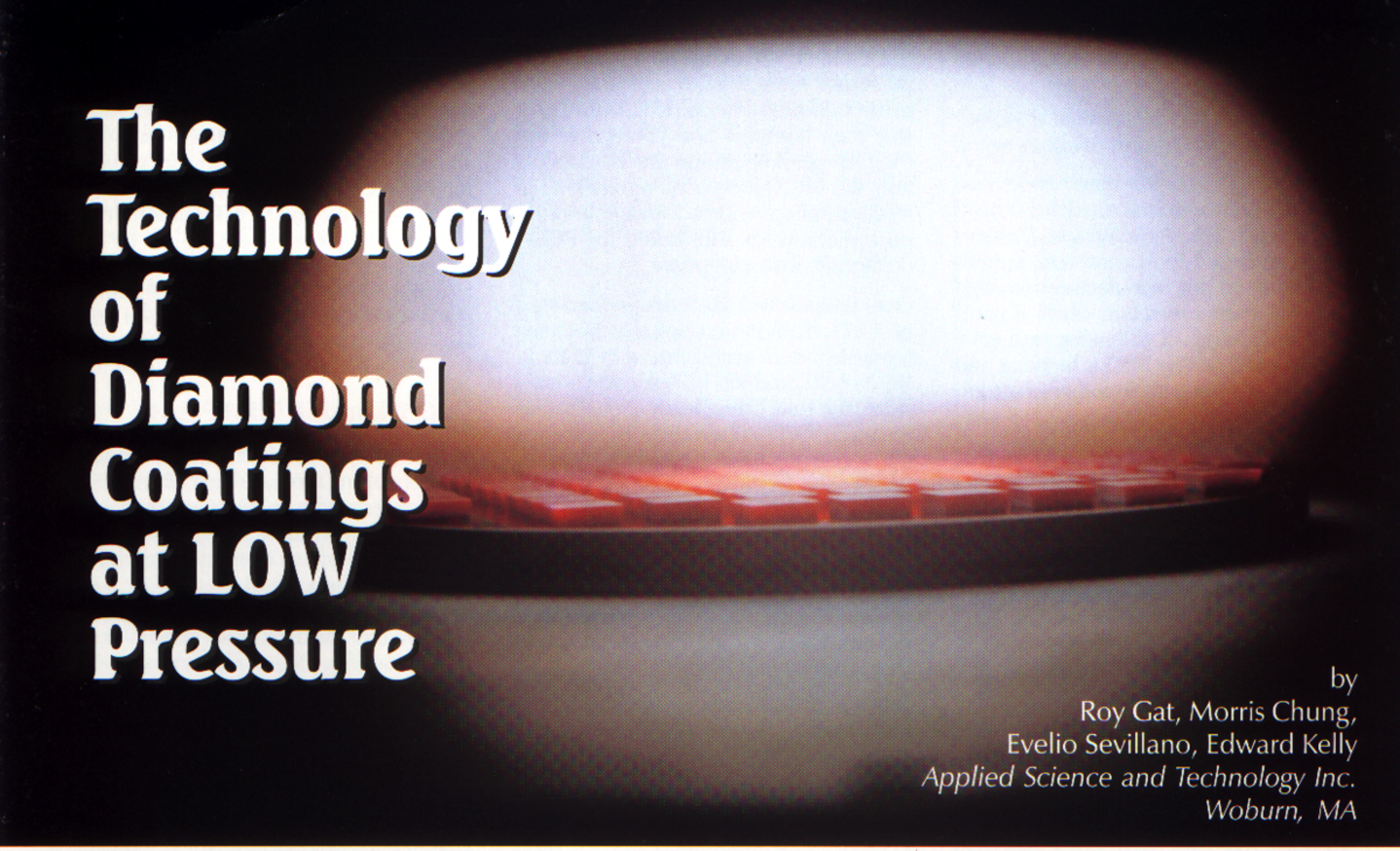

The Technology of Diamond Coatings at LOW Pressure

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Introduction

Over the last decade significant advances have been made in transforming a new kind of diamond production technology to a commercial reality. The technology is diamond Chemical Vapor Deposition (CVD). Today, CVD diamond products with remarkable properties can be found in the marketplace in products such as carbide tool coatings, heat spreaders for electronics, and optical windows. The potential for growth of this new industry remains outstanding with promising new applications in cellular phone technology, high power switching and ultimately in active electronics.

What is CVD Diamond

CVD diamond is an agglomeration of small (1-100 μm in diameter) single crystals of diamond. The material is often deposited on silicon or molybdenum in the shape of a free standing blank or wafer with thickness of the order of a millimeter. Each of the single crystals that constitute the wafer is virtually identical material to natural diamond but often of higher chemical purity. Each crystal is strongly bonded to its neighbours as evidenced by intra-granular fracture patterns. The diamond wafers can be laser cut into final shape or the substrate material can be shaped so that the diamond deposits in its final geometry.

Turn key micro-wave reactors capable of unattended diamond deposition over areas of up to 12" in diameter are commercially available (ASTeX, Woburn MA). The cost per carat of CVD diamond is sensitive to the total volume produced. In the largest commercially available reactor, the economics of scale depress the cost. The present cost per carat is under $10 and is projected to be under $4 by year end. A carat of diamond is 200 mg or approximately a piece of size 10x10x0.6 mm.

How CVD Diamond is Made

Making artificial diamond films at low pressures is remarkably simple. CVD diamond is made when a dilute mixture of methane (CH_4) in hydrogen is chemically excited to produce atomic hydrogen and hydro-carbon radicals. In most commercial systems excitation is performed using microwave radiation. Alternative techniques for gas excitation include oxyacetylene torch, DC arc-jet, RF discharges, and hot filaments among others. The microwaves partly ionize and cause intense heating of the gas mixture up to 4000°C. The diamond film is formed on a surface held at about 900°C in proximity to the excited gas. Typical pressures are sub-atmospheric (100 Torr) and growth rates are 15 μm/hr depending on reactor design and power.

The Markets for CVD Diamond

The main markets for CVD diamond currently include tool coatings, windows and heat sinks. Below we will ex-

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amine in more detail the requirements of these markets.

Tool Market

Diamond tools are not new. They have long filled an industry need for critical machining of abrasive materials. Until recently, diamond tools consisted of artificial diamond grit manufactured at high pressure and temperature which is compacted, with cobalt as binder, to a solid known as PCD. The PCD is then cut and brazed onto the cutting corner of a tool.

Many highly abrasive materials such as high silicon aluminum can only be machined economically using PCD or CVD diamond tools. A diamond coated tool can typically manufacture one to two *orders* of magnitude more parts than an uncoated tungsten carbide tool. Now, the technology of low pressure diamond deposition by CVD makes it possible to coat virtually any tool shape with a pure diamond coating.

CVD diamond tools were found to excel in cutting green (pre-fired) ceramics, fiber (e.g. graphite, glass) reinforced composites, copper alloys (e.g. brass, bronze), metal matrix composites (e.g. A359-Al/SiC, 6061-Al/Al_2O_3), magnesium alloys, plastics, laminates, and wood. Table I shows that the hardness of the particulates present in some of the aluminum alloys is on the order of carbide tool hardness. This leads to rapid tool failure when using uncoated carbide tools. Diamond, because of its extreme hardness has excellent performance in machining these abrasive materials.

Material	Knoop Micro-Hardness (GPa)
WC(Co)	14-18
TiN	18
Al_2O_3	21
TiC	25
SiC	25-30
CBN	30-93
Natural Diamond	75-115
PCD Diamond	50
CVD Diamond	31-65

Table I. Hardness of typical tool materials, tool coating materials, diamond coating and typical metal matrix composites particulates (SiC, Al2O3)

In the tool arena, users now have a "happy problem" of deciding when to use thick film CVD, thin film CVD or the traditional PCD tools.

CVD Diamond As Thick Film

An interesting new product is known as thick film CVD diamond or diamond sheet tool. Here, CVD diamond is grown to the thickness of a typical PCD (0.020"). It is then laser cut and brazed to the tool. Depending on the precise application, this substitution often results in a significant performance advantage because pure diamond is substituted for PCD's diamond/cobalt composite.

Over the past two years the performance of CVD diamond coatings has been extensively tested against that of PCD tools. While both products have specific advantages, the tests cited clearly show that on balance, CVD is significantly better in terms of being harder, more abrasion resistant, and more thermally conductive. Also, CVD diamond has a lower coefficient of friction and better chemical and thermal stability than PCD. PCD, however, leads in fracture strength. Table II qualitatively compares the relative material properties of CVD and PCD tools to their cutting performance.

CVD diamond Property (relative to PCD)	Benefit over PCD (* drawback)
Higher hardness	Precision cutting, slower wear
Conformal coating	Flexible tool geometries e.g. chip breakers
Smaller grain size	Finer surface finish
Higher abrasion resistance	Prolonged life, increased precision
Lower friction	Lower forces, lower heat generation, higher cutting speed
Higher rigidity	Increased precision
Higher chemical inertness	Cuts corrosive materials e.g.plastics
Higher thermal conductivity	Higher cutting speed
*Lower fracture strength	*Limited milling performance

Table II
A list of properties of diamond CVD coated tools as compared to PCD tools, and their relationship to machining.

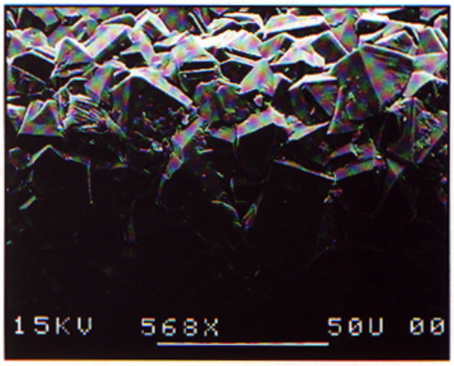
PCD is often bought by the tool manufacturer as a blank with a tungsten carbide backing. It is then cut by EDM into triangular tips (size 2-5mm). Each tip is open air brazed onto a tool corner. CVD diamond can also be bought as a wafer or blank. Without the cobalt metal, though, CVD diamond is an electric insulator and EDM cannot be used. Cutting is normally done with a laser. CVD diamond can be brazed to tungsten carbide in a vacuum furnace. Norton supplies CVD with carbide backing so that conventional brazing can be used.

There are some distinct manufacturing advantages to CVD thick films. The diamond is grown on a mirror smooth surface. Subsequent to deposition the diamond can be released from the substrate to yield mirror finish top surface for the tool tip. This obviates top polishing requirements. CVD diamond can be deposited over areas up to 12" in diameter. The versatility and affordability of laser cutting enables custom manufacturing of diamond cutting edges of practically any shape.

CVD Diamond Thin Films

In the thin film product, diamond coatings for cutting tools are typically 0.001" thick or less. The coatings are kept thin to maintain the cutting edge sharpness. The rake and flank of the tool are both coated. The diamond coating is conformal and allows the coating of chipbreaker designs and custom tool geometries. In CVD, all corners of the tool are diamond coated vs. only one corner. Thus, indexable CVD tools outperform alternative tools in tool life tests despite the dramatically thinner diamond layer. The promise of CVD is a cheap throwaway tool which offers excellent performance and which requires no resharpening of the diamond and the associated costly inventory and tracking problems.

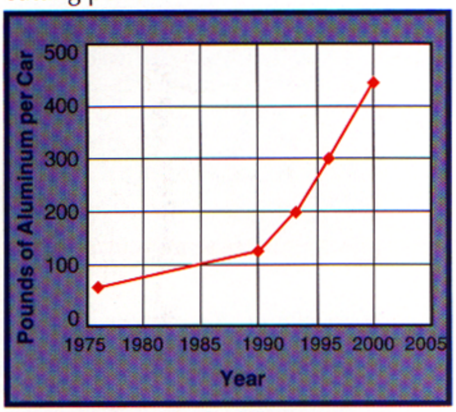
Adhesion of the coating to the underlying tool is a key requirement for competitive cutting performance and depends on the tool material. The adhesion of diamond coating to silicon nitride is excellent and CVD diamond coated silicon nitride tools outperform competitive tools in many cutting applications (e.g. machining graphite and polymer composites). Although diamond coating offers several key advantages, performance limitations which arise from tool bulk properties (e.g. fracture strength) still apply to the coated tool.



Diamond adhesion to binderless tungsten carbide (WC) tools is excellent leading to excellent cutting performance. The cobalt binder used in most tungsten carbide tools gives the tool its excellent fracture strength and without the binder, diamond coated WC tools are not as useful. Under CVD diamond growth conditions, the cobalt acts as a catalyst for the formation of weakly bonded carbon. This graphitic layer essentially eliminates the adhesion of the diamond to the tool.

Over the past several years several companies and research institutions found ways to improve the diamond adhesion. Several successful adhesion-promoting treatments have been reported and patented. Success has been limited to carbides with up to 6% cobalt (C2- grade). The most successful approach was to evaporate the cobalt from the surface layer while recrystallizing the surface grains to form a rough surface. It was found that removing the cobalt from the surface region (5-10 microns deep) is not significantly deleterious to the toughness, but dramatically increases the adhesion.

Today, almost all of the major carbide tool manufacturers have good adhesion technology for diamond on WC(Co). Tool life is now limited by diamond wear and not by delamination or spalling of the coating which provides excellent cutting performance.



Projected growth of aluminum use in automobile parts.

Economics of CVD Diamond Tools.

The world market for diamond-coated inserts based on estimates from large tool insert manufacturers is $150 million per year. Perhaps the fastest growing demand for diamond tools is in the automotive market. The projected growth of the aluminum content in automobiles is shown in the chart above. This increase is due in part to impending government regulation concerning fuel efficiency . Many of the alloys are hyper-eutectic which have highly abrasive silicon particulates in the aluminum bulk. These particulates are of comparable hardness to tungsten carbide and severely limit carbide tool life, yet, are machinable using diamond tools.

Cost per Carat of Diamond Coated Tools

For CVD diamond replacement of PCD tips, the end user has three choices for supply: he can buy finished tools (Norton, Northborough, MA), he can buy diamond blanks to cut and braze (Norton, ASTeX, CMC) or he can purchase a diamond deposition reactor and grow thick diamond films himself (ASTeX). An in-house program to make CVD diamond will cost the user about $9 per tool.

Cost analysis of an in-house thick film program is shown below. Here, the example uses production of 2.5" diameter, 480 micron thick diamond discs. Three deposition runs per week are assumed, at 48 hours each. Deposition is unattended except for loading and unloading the reactor. Reactor uptime of 85% is assumed, for a total of 6400 hrs/yr. Reactor price ($450k), facilities, space, labor, service, and other costs, the model yields a price of $64/carat, or $221/ square inch of diamond. After laser cutting, the disc yields 220 equilateral triangles with 5 mm sides. This equals 45 diamond tips per square inch, at a cost of $4.91 each. Laser cutting the diamond, pocketing the carbide, brazing the diamond, and grinding to shape will bring the price per tool up to about $9 plus the cost of the base carbide. No top polishing is required. In some applications CVD tools perform much better than competitive tooling, underlining the economic advantage of the new technology.

Thin Film Diamond Tool Coating

For thin-film CVD, the end user has three choices for supply:

1) Buy from one of several tool firms offering diamond coated tools (e.g., Crystallume, Kennametal, Norton (nitrides only), Sandvik, Teledyne).

2) Utilize a toll coating service such as Balzers, Crystallume or SP³. In this service, diamond coating is applied to tools supplied by the customer.

3) Purchase a diamond coating reactor for in-house coating. (ASTeX, Woburn MA).

Below is a breakdown of costs for in-house production (single reactor).

Annual production level[1]	10000 inserts
Annual operating costs	$125,000
Reactor price (AX6560)	$450,000
Diamond coating cost per insert	$12
Microwave power	8 kW
Batch size	28 inserts
Weight gain uniformity	15% or better
Deposition thickness	10 microns
Runtime including venting and loading	10 hours
Runs/day	2
Gas flow	600 sccm
Gas cost	$2000/yr
Facilities cost	$12,000
Electricity	$0.07/kWh
Magnetron life	5000 hours
Magnetron replacement price	$5000
Space (100 sq/ ft at $80/sq ft)(yr?)	$8000
Technician labor	2.5 hrs/day
Supervisor labor	1.3 hours/day
Labor overhead	150%
Est. labor cost	$25,000/yr

[1]based on a 50 week year, SPG 422 sized inserts, 90% up- time, and 80% yield.

Current Suppliers

Kennametal currently offers diamond coated tool inserts in the USA. Crystallume, a small business, sells tools independently and though distributors. Crystallume also offers toll coating services. Teledyne offers CVD diamond coated products and until recently relied on a small coating firm named SP³ for diamond coating. Sandvik's diamond coated tools are produced using Balzers proprietary equipment. Norton is offering a toll coating service and both thick and thin diamond coatings. Several Japanese companies are in process of developing tool coating technologies. ASTeX dominates the market for diamond coating equipment with over 200 units sold worldwide.

Two multi-million dollar NIST funded contracts have been awarded to support the development of reliable diamond coated round tools (drills and end mills). But such tools are not yet available. Notably, Nachi Fujikoshi from Japan is currently marketing diamond coated drills and other Japanese companies may soon join in.

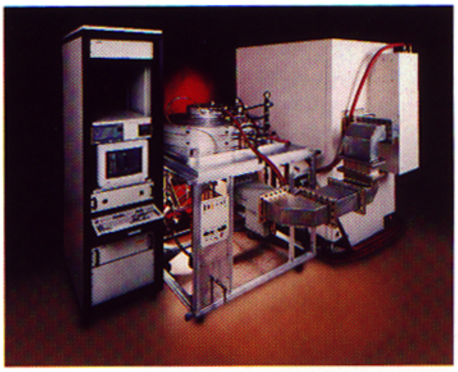
Window /Radome Market

Because CVD diamond is self supporting and not compacted with any additives, it has most of the outstanding optical properties of natural diamond. Diamond is transparent in a broad band all the way from the infrared to the ultraviolet. GE has patented transparent CVD diamond and is marketing CVD diamond windows for optical sensor applications.

The Army and Navy are developing CVDdiamond windows and radar domes for use in ultrafast (Mach 7) missiles. These windows are required to be transmissive to the infrared band used by the heat seeking detectors and to be resistant to extreme erosion and impact which occurs when the missile travels through a cloud or a dust storm. CVD diamond may provide a solution to this tough material problem.

Thermal Spreaders (Heat Sinks)

CVD diamond can be made with as high a thermal conductivity as natural diamond. Diamond at room temperature has the highest thermal conductivity of any material. As the packing density of electronic chips becomes higher, heat dissipation problems become tougher to solve. Once the cost of diamond production is reduced by a factor of about 4 as compared to the present level, CVD diamond may find wide-spread use as the semi-conductor chip heat sink material of choice. CVD diamond has already been applied to heat spreading in laser diodes used for fiber-optic communications.



Future Markets

Microwave Communication

There is a class of devices which manipulate microwave signals by converting them first into acoustic waves. These utilize surface acoustic waves and are hence called SAW devices. They include band pass filters, switchable filters with control of the transfer function, and resonators. They are used in TV broadcasting, transponders, and receivers, garage door openers, keyless car entry systems. The devices utilize a piezoelectric material to interchange between microwave and acoustic signals. By using CVD diamond as the acoustic medium the device benefits from the extraordinarily fast acoustic velocity in diamond (highest of any material) which permits higher microwave frequencies to be used.

Active Electronics

Diamond is a high bandgap semiconductor with very high carrier mobilities. A transistor or any other electronic device built in diamond could theoretically operate at much higher temperatures and at higher clock speeds than Si or GaAs devices. Today, preliminary work has already showed the feasibility of diamond diodes and FETs, however no-one as yet has been able to dope diamond 'n' type. Thus, when the formidable technological barrier to developing the integrated chip technology in diamond is passed, diamond may constitute the electronic chip of the future.

High Power Switching

An easier application is using diamond semiconducting properties as a high power switch. Being a semiconductor diamond can be made conductive by charge carrier injection. Injection is performed by irradiating diamond with electron beams. It is estimated that diamond can switch 100KW of power at MHz frequencies. High power switching is of primary importance to the high power electronic market and in military radar technology.

Conclusion

The concurrent improvement in CVD diamond deposition technology and the increasing demand for diamond tools have lead to new diamond coated tool products on the market. These include thin film coated carbide and nitride tools, PCD replacements and custom tools.

The availability of turn key diamond deposition reactors may enable small to medium sized tool companies to seize a chunk of the emerging new markets.

Today's CVD diamond technology has made diamond an engineering option in tool coating. The technology has a bright future ahead in a variety of applications when further reductions in the cost/ct are achieved. ◆

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