Trends and future for the emerging diamond deposition technology

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Diamond coatings, by virtue of their excellent properties, are expected to play a significant positive role in our lives. This review briefly covers the methods used for their preparation and characterization. A few typical applications of the diamond films are considered and explained. Status of the field, both in the international and national context, is elaborated with the contributions from the author's laboratory receiving a rather detailed description. Our perceptions regarding the future trends in the field are also described.

Diamond is endowed with extreme, unique and diverse properties and these can be seen as described in Table 1, to be always either a minima or maxima of the values for all materials for any given property. Also, the combination of high thermal conductivity and high electrical resistivity is rather rare. All these excellent properties have given rise to its large application potential with high economic stakes and this forms the chief motivation for the advancement of diamond related science and technology. Diamond is crystalline form of carbon and it occurs in nature. Its supply, however, is limited, uncertain and far below the demand, and this has fuelled efforts for its synthesis in the laboratory. First success for the same was achieved using the high pressure (~100 kbar) high temperature (~1400°C) method. The method is unable to deposit diamond thin films and coatings, which form more useful configuration for several important applications.

Deposition of Diamond Crystallites and Thin Films

Recently, several chemical vapour deposition methods have been developed for the purpose. The deposition process involves a gas phase chemical reaction occurring above a solid surface and is carried out at nearly atmospheric or sub-atmospheric pressure and at a substrate temperature of ~1000°C. Under these normally used conditions, although diamond is thermodynamically unstable, kinetics and presence of atomic hydrogen has been made to overtake thermodynamics. The synthesis of diamond obviously requires a source of carbon. Many carbonaceous gases

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### Table 1 — Various diverse properties exhibited by diamond

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom number density</td>
<td>$1.77 \times 10^{23}$/cm$^3$</td>
<td>Highest of any material at terrestrial pressure</td>
</tr>
<tr>
<td>Hardness</td>
<td>12,000-15,000 kg/mm$^2$ (Vickers)</td>
<td>Highest* intrinsic</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>$1.2 \times 10^{12}$ N/m$^2$</td>
<td>Highest</td>
</tr>
<tr>
<td>Room temp. thermal conductivity</td>
<td>20 W/cm K</td>
<td>Approx. 4 times of copper or silver</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>$\sim 10^{13}$ Ω cm</td>
<td>High</td>
</tr>
<tr>
<td>Band gap</td>
<td>5.45 eV</td>
<td>High</td>
</tr>
<tr>
<td>Dielectric Strength</td>
<td>$1 \times 10^6$ V/cm</td>
<td>Exceedingly high</td>
</tr>
<tr>
<td>Charge carrier velocity</td>
<td>$1 \times 10^7$ cm/sec for holes</td>
<td>Unsurpassed</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^7$ cm/sec for electrons</td>
<td></td>
</tr>
<tr>
<td>Radiation resistance</td>
<td>Radiation hard</td>
<td>Extremely low capture cross section for neutrons</td>
</tr>
<tr>
<td>Thermal co-efficient of expansion</td>
<td>$0.8 \times 10^{-6}$ at 300 K</td>
<td>Lower than even invar</td>
</tr>
<tr>
<td>Co-efficient of friction</td>
<td>0.1 in air</td>
<td>Low</td>
</tr>
<tr>
<td>Thermal shock resistance</td>
<td>---</td>
<td>Good</td>
</tr>
<tr>
<td>Sound propagation velocity</td>
<td>18.2 km/sec</td>
<td>High</td>
</tr>
<tr>
<td>Optical transmission</td>
<td>Wide range from $\lambda$=0.22-2.5 &amp; $&gt; 6 \mu$m</td>
<td>Superior. Resistant to all acids, bases and solvents at room temperature</td>
</tr>
<tr>
<td>Chemical inertness</td>
<td>Superior</td>
<td></td>
</tr>
</tbody>
</table>

*Recently, nano-composite coatings of nc-Ti N/a-Si N$_x$ with extrinsic hardness at least as high as that of the hardest diamond have been reported.

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such as hydrocarbons, alcohols, ketones, carbon oxides, carbon halides, etc., have been found to be suitable source gases. Carbon containing precursor molecules may be activated by thermal means (e.g. hot filament) or plasma (DC, RF or microwave) or combustion flame. The decomposed product is made to form a film on the substrate and the formation of non-diamond carbon is prevented by the presence of a selective etchant such as atomic hydrogen which etches away graphite around 100 times faster than diamond. Atomic hydrogen plays other important roles as well. High pressure (pressure ~ an atmosphere) methods normally give higher deposition rates compared to low pressure (pressure ~ sub-atmospheric) methods. However, here, the area that can be coated becomes smaller and lot of energy is input on the substrate which therefore requires elaborate cooling arrangement. A significant common trend observed in different methods used for diamond CVD is that the linear deposition rate increases with increase in the temperature of CVD gas phase.

The technologies for making diamond from the gas phase are categorized according to four basic methods, as described here.

(i) Hot filament chemical vapour deposition (HFCVD)

In this technique, generally a gaseous mixture of methane and hydrogen (1:99 v/v) falls on a refractory material (tungsten/tantalum/rhenium) filament heated to a temperature of around 2000 °C and the dissociated product is made to form a deposit on to the substrate (at ~850 °C) placed beneath the filament and at a distance of ~7-8 mm from it. The entire process is carried out at a pressure ~40 torr. The deposition rate for high quality diamond deposit is ~1 µm/h. Fig.1 shows a schematic diagram of a jet flow HFCVD facility, indigenously set up at the author's laboratory, to uniformly coat up to 4" diameter substrate with unambiguously characterised polycrystalline diamond films. Multiple small sized substrates, coming within the area can be coated as well.

(ii) Plasma assisted chemical vapour deposition

Many plasma sources, such as radio frequency, microwave and direct current have been perfected for diamond deposition. In microwave CVD, one normally employs a quartz reactor tube having provision for pumping as well as introduction of the required gas in a controlled way. Microwave power (frequency 2.2 GHz), produced by magnetron, travels in a waveguide and is coupled, using an applicator, to the gas mixture inside the tube so as to form a ball shaped plasma. The substrate is placed at the lower end of the plasma ball and has provision for its temperature control. Under appropriate conditions, one may deposit diamond. Of late, several variants of the apparatus such as employing metal chamber, microwave torch, etc. have come into vogue.

(iii) Plasma jet methods

Herein, one uses a plasma jet torch (such as is used in welding and cutting) with hydrogen, methane and argon as source gas (at atmospheric pressure) to form diamond deposit on a substrate. Plasma is ignited by direct current or radio frequency and plasma temperature rises above 10,000 K. The substrate is cooled by water to limit its surface temperature to a safe value of a few hundred °C.

(iv) Combustion flame method

In this method, an ordinary welding or cutting torch is employed. Oxygen and acetylene are mixed in suitable proportion and the torch is lighted, with the reducing acetylene feather directed on the substrate, which is water-cooled. Under appropriate conditions, it is possible to deposit diamond. The method gives high deposition rate and can be carried out in ambient environment involving almost no capital cost. Fig. 2 shows a schematic diagram of a rotating, water...
Comparison of Different CVD Methods for Diamond Deposition

Detailed comparison of the methods can be found elsewhere. The choice of the method, in actual practice, depends on the specific requirement of the final product. For example, for coating tools or three-dimensional objects, HFCVD is probably a good choice. For optical and electronic applications of CVD diamond films, contamination from the vapours of the filament material is of concern. Here, microwave CVD is more suitable. Bulk polycrystalline diamond pieces for heat sink applications are more easily fabricated with a high rate deposition technique that utilises dc or rf thermal plasma torch or by means of an oxy-acetylene flame.

Characterisation

A material must meet three requirements before it can be called diamond, viz.: (i) It should have crystalline surface morphology which may be checked using scanning electron or transmission electron microscopy; (ii) It should be single phase and have characteristic ‘d’ spacing corresponding to that of diamond which may be checked using X-rays or electron diffraction; and, (iii) It should show the characteristic 1332 cm⁻¹ laser Raman line, which has been taken as signature of diamond. Electron energy loss spectroscopy has also been employed for the characterisation.

Typical Applications

Different diamond applications are based on some of its specific properties or their appropriate combination. Cutting tools, abrasive structural components and bearings are thus based on its mechanical, thermal and chemical properties; X-Ray, IR, laser windows and radomes, in addition, make use of its appropriate optical properties. High speed, high density, high temperature, radiation hard electronics, on the other hand, are mainly dependent on its suitable electronic, thermal and chemical properties.

Presently, IR windows for missile and tactical aircraft, periscope windows, diamond transistors and integrated circuits, medical implants, etc. are low volume, high value added products. X-ray windows, X-ray masks, heat sinks for electronics, and tribological and corrosion resistant coatings are medium volume, medium value added products while diamond coated cemented carbide tools, diamond capacitors, magnetic hard disc coatings, etc. come under high volume, low value added products.

At the moment, high quality loudspeakers that include diamond coated tweeters and mid-rangers can be considered amongst the applications already realized. These give distortionless sound reproduction down to the highest frequencies audible to the human ear. Amongst the applications in the take off stage, diamond coated cemented tungsten carbide, silicon nitride or silicon oxy-nitride tool inserts are already being marketed. These are particularly suitable for high speed dry cutting of non-ferrous metals and alloys and have increased tool life by several folds. Economically competitive heat sinks for thermal management of high power electronics, in sizes up to ~ 25 mm x 25 mm are being produced employing high rate CVD processes. Windows, transparent to IR, X-rays, high power lasers and operating under severe conditions of temperature, pressure differential and reactivity, have become available. One such window used on the spacecraft Pioneer while exploring the planet Venus, could successfully withstand the very severe environment comprising of 1% sulphuric acid, 450°C temperature and ninety atmosphere pressure differential. These windows are able to transmit soft X-rays and therefore, are being used in EDAX for the analysis of low atomic number elements. Recently, it
has become possible to give protective diamond coatings to large area (8-10 inches diameter) infra red windows (particularly ZnS) which should allow it to better withstand aerodynamic heating and erosion by airborne sand or rain for aerospace applications\textsuperscript{13}. These are expected to find applications in IR imagers and sensors which are being increasingly used for military applications in fighter aircrafts, missiles, night warfare equipment, etc. Prosthetic diamond coated implants, which are more compatible to body tissue, have found use in surgical procedures. Electronic applications, at the moment, may be considered still several years down the road. Diamond semiconducting devices, which are a new generation of devices, are expected to revolutionize the micro-electronic industry and are of utmost importance to defence and space programme. Thus, ultrafast supercomputers, extremely rapid and compact communication systems and devices which can operate inside running jet engines and nuclear reactors are awaiting advances in diamond thin film research. In spite of several impending difficulties, prototype thermistors\textsuperscript{14}, piezo-resistors\textsuperscript{15} and transistors\textsuperscript{15}, etc. have already been demonstrated employing even polycrystalline CVD diamond films.

An interesting potential application of CVD diamond (because of its negative electron affinity) is to use it as an electron emitter in flat panel displays. Such cathodes, using nitrogen doping\textsuperscript{16} and giving adequate emission current at low threshold voltages have been fabricated\textsuperscript{16}. Since these devices consume very low power, they are extremely efficient. Unlike liquid crystal displays, these will have high brightness, a large viewing angle and ability to be scaled up to large sizes (may be even meters square)!\textsuperscript{19}

**Status of the Field at International Level**

Multinational giants, defence and space related organisations in advanced countries are pumping in enormous amount of funds in diamond related research and technology so as to become key players in this strong field. Most of the crucial innovations are a closely guarded and proprietary in nature. Nonetheless, the research worldwide is directed towards growing better quality films, at higher rates, on to larger area substrates, at lower temperatures and with as good a uniformity as possible. Simultaneously, efforts are being made to grow reasonably large, defect free, single crystal films for electronic applications. Presently, the substrates range from metals to semiconductors to insulators and from glasses to single crystals; the lower temperature limit has dropped from around 1000°C to \textasciitilde 100°C and deposition rates have increased to \textasciitilde 1 mm/sec.

**Recent exciting developments**

Acetylene, which forms the major raw material cost component, in oxy-acetylene flame method, has recently been replaced by propylene with a cost reduction by roughly a factor of six\textsuperscript{18}. A non-corrosive, stable fluorine rich molecule, i.e. perfluorinated alkyl iodide, has been developed for the florrination of diamond thin film surface so as to make it relatively frictionless\textsuperscript{19}. This simple new method is expected to help engineers design slippery low friction tools and devices that work under a wide range of temperatures.

To increase the diamond growth rates, novel substrate designs have been proposed by Partridge et al.\textsuperscript{20} that exploit three-dimensional arrays of small diameter wires or fibres. The resulting increase in substrate area per unit volume, increases the mass of the diamond deposited per unit time by orders of magnitude with no increase in the net gas flow or power consumption. The idea is expected to reduce the manufacturing cost for thicker composite sections by orders of magnitude, thereby leading to substantial reductions in the cost of diamond fibre composites.

**New methods**

The low pressure solid state source process (LPSSS), developed recently\textsuperscript{21}, converts under appropriate conditions, a solid source of carbon into diamond at a pressure \textasciitilde 1 atm atmosphere. In this technique, fine powders of solid carbon and an appropriate metal (or alloy or its hydride) are intimately mixed, pressed into a pellet and exposed to atomic hydrogen. Excess carbon in `MCH` eutectic, so formed, precipitates out as diamond. Even epitaxial growth has been demonstrated with a deposition rate of \textasciitilde a few μm/h.

A new technique\textsuperscript{22,23}, using three or four different wave length, pulsed synchronised lasers and working in an ambient environment of carbon dioxide-nitrogen gas mixture, has opened up a cheap, fast and less energy intensive way of coating objects with diamond at a `body' temperature of less than 100°C. Herein, the plasma generated at a small spot on the surface of the sample, heats the surface to very high temperature of \textasciitilde 10,000°C, which creates the diamond crystal lattice and bonds it to the surface. Since the mass
temperature of the substrate is low, it restricts the metallurgical activity to the substrate surface only. Thus, the substrate coating bond is metallurgical and there are no sacrifices on the substrate toughness. The object is moved, using a robot arm, so as to bring its different portions in the coating area. Deposition rates are very high ~ 1 μm/sec. and coating as thick as 1 mm has been deposited without its getting delaminated. The technique has aroused lot of interest in the U.S. motor industry, medical works and defence. There are reports that General Motors have already tied up with the inventors for coating automobile gear boxes with diamond and the military funding them for coating helicopter blades with diamond to protect them with the sort of conditions they endured during the gulf war, when blasting by sand in the air caused serious damage. Gillette company is exploring the possibility to coat their blades with diamond.

**Status of the Field at National Level**

Laboratory scale facilities for diamond deposition such as HPCVD (Poona University; IIT, Delhi; IIT Bombay; BARC; NAL, Bangalore), MWCVD (IIT, Delhi; IIT, Bombay), Oxy-acetylene flame (BARC; IIT, Delhi), and axial magnetron sputtering (IACS, Calcutta) have been set up, primarily for academic purpose and not much headway seems to have been made as far as applications are concerned. Highlights of the contributions from our group are summarised here. An innovative modification of 'jet-flow' along with high flow rates of input gaseous mixture, has been introduced in HPCVD technique which has enabled to increase the filament to substrate distance and coat diamond on three dimensional comparatively large sized odd shaped substrates, both inside as well as outside. Using this modified technique, methodology has been developed, to form phase pure exotic diamond shapes such as self-supporting diamond tube, self-supporting hollow diamond helix and self-supporting diamond sieve. This is a big achievement considering the difficulties encountered in shaping diamond. These shapes, endowed with extreme and exceptional diamond properties are expected to find several high tech. applications. We could fabricate MIS structures using polycrystalline diamond film as an insulator, Si (100) as semiconductor and titanium as metal contact. These structures are not appreciably affected when exposed to 1 Mrad of γ-rays and are temperature stable up to 200°C. The diamond films could also be doped \textit{in situ} with boron so as to show \textit{p}-type semiconducting behaviour. We could make diamond coated cutter which efficiently cuts glass slides and silicon wafers. Diamond coating on tube cutter wheels showed improved performance. Also, cobalt cemented tungsten carbide tool inserts of different types, when coated with diamond, show under actual production conditions: (i) 100-fold increase in tool life for high speed machining (cutting speed = 800 m/min, feed = 0.15 mm/rev., depth of cut = 1.5 mm) of LM 24 aluminium alloy wheels and give very good surface finish to the job, and (ii) an increase of 25 per cent in tool life for high speed machining (cutting speed = 80 m/min, feed = 0.15 mm/rev.; depth of cut = 1mm on both OD & ID) of cast iron piston ring stacks.

**Perceptions about Future Developments**

1. Diamond growth mechanism will be more fully understood and more realistic models of gas phase species densities and flow dynamics will be formulated. Recent investigations employing methane-argon gas mixture (i.e. no molecular hydrogen) and standard microwave plasma conditions, have shown C2 to be the predominant species present and the resulting deposit to be nanocrystalline diamond. The improved models will form the basis of future 'smart' process monitoring and control schemes which, using noninvasive probes will ensure maximisation of the flow of diamond precursors to the substrate surface while minimising the competing deposition of non-diamond carbon films.

2. It may become possible to grow reasonably large sized, defect free, heteropitaxial diamond films directed towards electronic applications.

3. Low pressure solid state source technique could become of major significance. This could make possible the development of new and improved routes to grow gems and single crystals including fibres.

4. The novel pulsed multiple laser technique appears to have really produced a revolution and if the claims made by its proponent are proved correct, it could knock the new CVD diamond industry on its head.

5. Diamond coatings are expected to make so large an impact in near future that many people believe that future age will be known as 'diamond age' going chronologically from the 'stone age' to 'bronze age', to 'iron age' of the past and 'silicon age' of the present.
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References